Journal of Organometallic Chemistry, 238(1982)1 - 78
Elsevier Sequoia S.A., Lausanne - Printed in The Netherlands

Review

PREPARATION, PROPERTIES AND APPLICATIONS OF ORGANOSILICON PEROXIDES

Yu.A. ALEXANDROV
Chemistry Institute, Lobachevsky State University, Gagarin
Avenue 23, Gorky, 603600, USSR

CONTENTS

INTRODUCTION

Organosilicon peroxides are among the best known of the organoelement peroxides. The advances in this field of organoelement chemistry are well covered in the recent reviews dealing with or-

0022-328X/82/0000-0000/$19.50

ganic peroxides of non-transition elements of the first (ref. 148), second (ref. 8), third and fourth (ref. 10) groups.

The chemistry of organic peroxides of the silicon subgroup elements also is covered in a number of reviews and monographs, directly or indirectly (ref. 3, 4, 31, 56, 42, 126, 127, 132, 149).

The publication of the present review is timely, as in recent years systematic investigations of organosilicon peroxides have resulted in a rather extensive accumulation of data concerning the preparation properties and applications of these compounds.

METHODS OF SYNTHESIS

Organosilicon hydroperoxides, R_3SiOOH

R_3SiOOH-type hydroperoxides are obtained by reaction of the appropriate organosilicon chloride with hydrogen peroxide in an organic solvent in the presence of agents which can scavenge the hydrogen chloride evolved (organic and inorganic bases).

$$R_3SiCl + H_2O_2 \rightarrow R_3SiOOH + HCl \qquad 1.1$$

$$HCl + NH_3 \text{ (for example)} \rightarrow NH_4Cl \qquad 1.2$$

In this manner first Me_3SiOOH and Et_3SiOOH (ref. 22, 74) and then a series of other organosilicon hydroperoxides were obtained (Table 1, comp. 1-7).

Organosilicon hydroperoxides with two and more hydroxy-groups on silicon have not been described. Such polyhydroperoxides seem to be unstable.

Organosilicon peroxides, $R_{4-n}Si(OOR')_n$

Synthesis by reaction of organosilicon halides with organic hydroperoxides and their alkali metal salts. The general method of synthesis of $R_{4-n}Si(OOR')_n$ peroxides involves a reaction of the appropriate $R_{4-n}SiX_n$ organosilicon halide (in most cases chlorides) with hydroperoxides (R'OOH). The reaction is reversible. It proceeds in inert organic solvents at room temperature or below and in the presence of agents which are capable of binding the hydrogen halide which is evolved.

For example:

$$R_3SiCl + R'OOH \rightleftharpoons R_3SiOOR' + HCl \qquad 1.3$$

$$HCl + NH_3 \rightarrow NH_4Cl \qquad 1.4$$

(Continued on p. 29)

TABLE 1

Organosilicon peroxide compounds

Nº	Peroxide	Method of production	Yield p.c.	T_{melt} °C	T_{boil} Hg mm	d_4^{20}	n_D^{20}	Ref.
1	2	3	4	5	6	7	8	9
1	$(CH_3)_3SiOOH$	$(CH_3)_3SiCl + H_2O_2$ base						22.74
2	$(C_2H_5)_3SiOOH$	$(C_2H_5)_3SiCl + H_2O_2$ base						22
3	$(C_6H_5)_3SiOOH$	$(C_6H_5)_3SiCl + H_2O_2$ base	56	110-112				22.54.177
4	$CH_3(C_6H_5)_2SiOOH$	$CH_3(C_6H_5)_2SiCl + H_2O_2$ base	54	40-41				54
5	$(C_6H_5CH_2)_3SiOOH$	$(C_6H_5CH_2)_3SiCl + H_2O_2$ base	63	60-61				54
6	$(n\text{-}C_6H_{13})_3SiOOH$	$(n\text{-}C_6H_{13})_3SiCl + H_2O_2$ base	83				1.4550	54
7	$(p\text{-}CH_3C_6H_4)(C_6H_5)_2SiOOH$	$(p\text{-}CH_3C_6H_4)(C_6H_5)_2SiCl + H_2O_2$ base	62.5	75				138
8	$(CH_3)_3SiOOC(CH_3)_3$	$(CH_3)_3SiCl + (CH_3)_3COOH$	54		41/41		1.3933	74.84.139
			89		79/215	0.8219/25	1.3935/25	57.58
			91		114 (decomp.)			59.70
		$(CH_3)_3SiNHR + (CH_3)_3COOH$						119

1	2	3	4	5	6	7	8	9
		$(CH_3)_3SiN(CH_3)_2$+ $(CH_3)_3COOH$ trifluoroacetic acid						116
9	$(CH_3)_3SiOOC_3H_{7-n}$	$(CH_3)_3SiCl$ + n-C_3H_7OOH	91		42/50		1.3948	31
10	$(CH_3)_3SiOOC_4H_{9-n}$	$(CH_3)_3SiCl$ + n-C_4H_9OOH base	89.5		46/35 50/30		1.4013 1.4060	31 155
11	$(CH_3)_3SiOOC_4H_9$-sec	$(CH_3)_3SiCl$ + sec-C_4H_9OOH base			46/35		1.4038	155
12	$(CH_3)_3SiOOC(CH_3)_2C_2H_5$	$(CH_3)_3SiCl$ + $C_2H_5(CH_3)_2COOH$ base	84 89		78/95 52/1	0.8419/25 0.916	1.4032/25 1.4495	57-59 115
13	$(CH_3)_3SiOOC_{10}H_{11}$	$(CH_3)_3SiCl$ + $C_{10}H_{11}OOH$ base	98		53/0.01		1.5102/25	57-59
14	$(CH_3)_3SiOOC(CH_3)_2C_6H_5$	$(CH_3)_3SiCl$ + $C_6H_5(CH_3)_2COOH$ base	53 75		43/0.05 176 (decomp.)	0.9501/25	1.4780/25	58.59 70
		$(CH_3)_3SiN(CH_3)_2$ + + $(C_6H_5)(CH_3)_2COOH$ trifluoroacetic acid						116
15	$(CH_3)_3SiOOC(CH_3)(C_6H_5)_2$	$(CH_3)_3SiCl$ + $(C_6H_5)_2(CH_3)COOH$ base	80-90	61.5-62				151.165
16	$(CH_3)_3SiOOCH(CH_3)C_6H_5$	$(CH_3)_3SiCl$ + $C_6H_5(CH_3)HCOOH$ base			45/0.06		1.4796	161
17	$(CH_3)_3SiOOCH(C_6H_5)_2$	$(CH_3)_3SiCl$ + $(C_6H_5)_2CHOOH$ base					1.5340	19.155
18	$(CH_3)_3SiOOC(C_6H_5)_3$	$(CH_3)_3SiCl$ + $(C_6H_5)_3COOH$ base	80	60-62				151.165

1	2	3	4	5	6 7	8	9
19	$(C_2H_5)_3SiOOC(CH_3)_3$	$(C_2H_5)_3SiBr$ + $(CH_3)_3COOH$ base	57 52 74		44-45.5/1 44-45/1 175(decomp.) 38-40/0.05	1.4198 1.4178	13.15 129 70 84
20	$(C_2H_5)_3SiOOC(CH_3)_2C_6H_5$	$(C_2H_5)_3SiCl$ + adduct $(C_6H_5)(CH_3)_2COOH$ with amine	80		43/0.05		70
21	$(n\text{-}C_4H_9)_3SiOOC(CH_3)_3$	$(n\text{-}C_4H_9)_3SiCl$ + $(CH_3)_3COOH$ base	95		170(decomp.)		70
22	$(n\text{-}C_4H_9)_3SiOOC(CH_3)_2C_6H_5$	$(n\text{-}C_4H_9)_3SiCl$ + adduct $C_6H_5(CH_3)_2COOH$ with amine	95		157(decomp.)		70
23	$(CH_3)_2C_6H_5SiOOC(CH_3)_3$	$C_6H_5(CH_3)_2SiCl$ + $(CH_3)_3COOH$ base			40/0.05 58/1	1.4762/25 1.4779	58 144
24	$(CH_3)_2C_6H_5SiOOC(CH_3)_2C_6H_5$	$C_6H_5(CH_3)_2SiCl$ + $C_6H_5(CH_3)_2COOH$ base	93		215(decomp.)		70
25	$(CH_3)(C_6H_5)_2SiOOC(CH_3)_2C_6H_5$	$CH_3(C_6H_5)_2SiCl$ + $C_6H_5(CH_3)_2COOH$ base	93 95	50 62	177(decomp.) 205(decomp.)		70 165
26	$(C_2H_5)_3SiOOCH(CH_3)C_6H_5$	$(C_2H_5)_3SiCl$ + $C_6H_5(CH_3)$ CHOOH base			63-64/0.05	1.4852	161
27	$(n\text{-}C_3H_7)_3SiOOCH(CH_3)C_6H_5$	$(n\text{-}C_3H_7)_3SiCl$ + $C_6H_5(CH_3)$ CHOOH base			78/0.05	1.4800	161
28	$(C_6H_5)_3SiOOC(CH_3)_3$	$(C_6H_5)_3SiCl$ + $(CH_3)_3COOH$ base	95		205(decomp.)		57.58.70
29	$(C_6H_5)_3SiOOC(CH_3)_2C_6H_5$	$(C_6H_5)_3SiCl$ + $C_6H_5(CH_3)_2$ COOH base	85 70	68-69 72	220(decomp.)		165.178 70

1	2	3	4	5	6	7	8	9
30	$(C_6H_5)_3SiOOC(CH_3)(C_6H_5)_2$	$(C_6H_5)_3SiCl + CH_3(C_6H_5)_2COOH$ base	80	90–91				165.178
31	$(C_6H_5)_3SiOOC(C_6H_5)_3$	$(C_6H_5)_3SiCl + (C_6H_5)_3COOH$ base	96 82	198–199 162–163				36 165.178
32	p- $[(CH_3)_3SiOOC(CH_3)_2]_2$	$(CH_3)_3SiCl$ + p- $HOOC(CH_3)_2$ 2 C_6H_4 base		71–72				106
33	$C_2H_5(CH_3)_2SiOOC(CH_3)_3$	$C_2H_5(CH_3)_2SiCl + (CH_3)_3COOH$ base	70		70/60		1.4069	144
34	$C_3H_7(CH_3)_2SiOOC(CH_3)_3$	$C_3H_7(CH_3)_2SiCl + (CH_3)_3COOH$ base	75		50/13		1.4072	144
35	$C_4H_9(CH_3)_2SiOOC(CH_3)_3$	$C_4H_9(CH_3)_2SiCl + (CH_3)_3COOH$ base	65		45/6		1.4140	144
36	$C_6H_5CH_2(CH_3)_2SiOOC(CH_3)_3$	$C_6H_5CH_2(CH_3)_2SiCl + (CH_3)_3COOH$ base	72		79/1		1.4806	144
37	$(CH_3)_2Si[OOC(CH_3)_3]_2$	$(CH_3)_2SiCl_2 + (CH_3)_3COOH$ base	76		40/1 185 (decomp.)	0.9415/25	1.4149/25	59 70
			70		34.5–35/1	0.905	1.4087	19.115
38	$(CH_3)_2Si[OOC(CH_3)_2C_6H_5]_2$	$(CH_3)_2SiCl_2 + C_6H_5(CH_3)_2COOH$ base	85		142 (decomp.)			70
			80		120/0.03	0.976	1.4681	115
39	$(C_6H_5)_2Si[OOC(CH_3)_2C_6H_5]_2$	$(C_6H_5)_2SiCl_2 + C_6H_5(CH_3)_2COOH$ base	80			1.048	1.5338	115
				55.3–57.4				140

1	2	3	4	5	6	7	8	9
40	$(CH_3)(C_6H_5)Si[OOC(CH_3)_3]_2$	$(CH_3)(C_6H_5)SiCl_2$ + $(CH_3)_3COOH$ base	70		70/0.02	0.985	1.4703	115
41	$(CH_3)(C_6H_5)Si(OOC_5H_{11}\text{-}t)_2$	$CH_3(C_6H_5)SiCl_2$ + t-$C_5H_{11}OOH$ base	73		80/0.02	0.978	1.4748	115
42	$(C_2H_5)_2Si[OOC(CH_3)_3]_2$	$(C_2H_5)_2SiCl_2$ + $(CH_3)_3COOH$ base	60		40/1		1.4149/25	57–59
		$(C_2H_5)_2SiF_2$ + $(CH_3)_3COOH$ base	62		54/1	0.908	1.4197	115
43	$(C_2H_5)_2Si(OOC_5H_{11}\text{-}t)_2$	$(C_2H_5)_2SiCl_2$ + $C_5H_{11}OOH$ base	73		40/0.02	0.906	1.4280	115
44	$H(CH_3)Si[OOC(CH_3)_3]_2$	$H(CH_3)SiCl_2$ + $(CH_3)_3COOH$ base	59		41–2/2	0.912	1.4070	115
45	$H(CH_3)Si(OOC_5H_{11}\text{-}t)_2$	$H(CH_3)SiCl_2$ + t-$C_5H_{11}OOH$ base	31		64–5/3	0.924	1.4205	115
46	$H(C_2H_5)Si[OOC(CH_3)_3]_2$	$H(C_2H_5)SiCl_2$ + $(CH_3)_3COOH$ base	59		50/2	0.921	1.4128	115
47	$H(C_2H_5)Si(OOC_5H_{11}\text{-}t)_2$	$H(C_2H_5)SiCl_2$ + t-$C_5H_{11}OOH$ base	50		40/0.02	0.939	1.4245	115
48	$(CH_3)_2Si(OOC_4H_9\text{-}sec)(OOC_4H_9\text{-}t)$	$(CH_3)_2Si(OOC_4H_9\text{-}t)Cl$ + + C_4H_9-sec OOH base	80		46.5–47.1	0.908	1.4113	113
49	$(CH_3)_2Si(OOC_5H_{11}\text{-}t)(OOC_4H_9\text{-}t)$	$(CH_3)_2Si(OOC_4H_9\text{-}t)Cl$ + + t-$C_5H_{11}OOH$ base	89		47–48.1	0.911	1.4140	113

1	2	3	4	5	6	7	8	9
50	$(C_2H_5)_2Si(OOC_4H_9\text{-}t)$ $(OOC_5H_{11}\text{-}t)$	$(C_2H_5)_2Si(OOC_4H_9\text{-}t)Cl$ + $t\text{-}C_5H_{11}OOH$ base	88		35/0.03	0.9072	1.4227	113
51	$(CH_3)_2Si(OOC_4H_9\text{-}t)OOC$ $(CH_3)_2C_6H_{11}$	$(CH_3)_2Si(OOC_4H_9\text{-}t)Cl$ + + $C_6H_{11}(CH_3)_2COOH$ base	80		64-65/0.02	0.9577	1.4452	113
52	$\{(CH_3)_2C[OOSi(CH_3)_3]CH_2\}_2$	$(CH_3)_3SiN(CH_3)_2$ + + $[(CH_3)_2C(OOH)CH_2]_2$ trifluoroacetic acid						116
53	$(C_6H_5)_2Si[OOC(CH_3)_3]_2$	$(C_6H_5)_2SiCl_2$ + $(CH_3)_3COOH$ base	89		110/0.01 165 (decomp.)	1.033/25	1.5103/25	57-59 70
54	$(CH_3)(C_6H_5)Si(OOC_4H_9\text{-}t)$ $(OOC_5H_{11}\text{-}t)$	$(CH_3)(C_6H_5)Si(OOC_4H_9\text{-}t)Cl$ + $t\text{-}C_5H_{11}OOH$ base	92		71.5/0.02	0.9178	1.4748	113
55	$(CH_3)Si[OOC(CH_3)_3]_3$	CH_3SiCl_3 + $(CH_3)COOH$ base	78		50/0.1 150 (decomp.)		1.4097	57-59 70
56	$C_6H_5Si[OOC(CH_3)_3]_3$	$C_6H_5SiCl_3$ + $(CH_3)_3COOH$ base			100/3.10-4		1.4882	143
57	$HSi[OOC(CH_3)_3]_3$	$HSiCl_3$ + adduct $(CH_3)_3COOH$ with amine	55		120 (decomp.)			70
58	$(CH_3)Si[OOC(CH_3)_2C_6H_5]_3$	CH_3SiCl_3 + $C_6H_5(CH_3)_2COOH$	83 57		100 (decomp.)	1.014	1.4780	115 70
59	$n\text{-}C_6H_{13}Si[OOC(CH_3)_3]_3$	$n\text{-}C_6H_{13}SiCl_3$ + adduct $(CH_3)_3COOH$ with amine	76		164 (decomp.)			70

1	2	3	4	5	6	7	8	9
60	n-$C_6H_{13}Si[OOC(CH_3)_2C_6H_5]_3$	n-$C_6H_{13}SiCl_3$ + adduct $C_6H_5(CH_3)_2COOH$ with amine	95		151 (decomp.)			70
61	n-$C_{12}H_{25}Si[OOC(CH_3)_3]_3$	n-$C_{12}H_{25}SiCl_3$ + adduct $(CH_3)_3COOH$ with amine	90		155 (decomp.)			70
62	n-$C_{12}H_{25}Si[OOC(CH_3)_2C_6H_5]_3$	n-$C_{12}H_{25}SiCl_3$ + adduct $C_6H_5(CH_3)_2COOH$ with amine	95		152			70
63	$C_6H_5Si[OOC(CH_3)_2C_6H_5]_3$	$C_6H_5SiCl_3$ + adduct $C_6H_5(CH_3)_2COOH$ with amine	61		20 (decomp.)			70
64	$Si[OOC(CH_3)_3]_4$	$SiCl_4 + (CH_3)_3COOH$ base	64	53	135			19.57–59 70
65	$Si[OOC(CH_3)_2C_6H_5]_4$	$SiCl_4$ + adduct $C_6H_5(CH_3)_2COOH$ with amine	64		100 (decomp.)			70
66	$(CH_2{=}CH)(CH_3)_2SiOOC(CH_3)_3$	$(CH_2{=}CH)(CH_3)_2SiCl$ + + $(CH_3)_3COOH$ base			35/13	0.849	1.4133	101
67	$(CH_2{=}CH)Si(CH_3)(C_2H_5)OOC(CH_3)_3$	$(CH_2{=}CH)(CH_3)(C_2H_5)SiCl$ + + $(CH_3)_3COOH$ base	58		31/4	0.8565	1.4206	101.188
68	$(CH_2{=}CH)(CH_3)(n\text{-}C_3H_7)SiOOC(CH_3)_3$	$(CH_2{=}CH)(CH_3)_3(n\text{-}C_3H_7)SiCl$+ + $(CH_3)_3COOH$ base			65/12	0.8621	1.4290	101
69	$(CH_2{=}CH)(CH_3)(C_2H_5)SiOOC_5H_{11}$-t	$(CH_2{=}CH)(CH_3)(C_2H_5)SiCl$ + + t-$C_5H_{11}OOH$ base	59		38/1–2	0.876	1.4308	188.99. 101

1	2	3	4	5 6	7	8	9
70	$(CH_2=CH)(CH_3)(C_2H_5)Si$ $OOC(CH_3)_2C_6H_5$	$(CH_2=CH)(CH_3)(C_2H_5)SiCl$ $C_6H_5(CH_3)_2COOH$ base	43	55/0.01	0.9656	1.4910	
71	$(CH_2=CH)(C_6H_5)_2Si$ $OOC(CH_3)_2C_6H_5$	$(CH_2=CH)(C_6H_5)_2SiCl$ + adduct $C_6H_5(CH_3)_2COOH$ with amine	92	155 (decomp.)			70
72	$(CH_2=CH)(CH_3)Si\left[OOC(CH_3)_3\right]_2$	$(CH_2=CH)(CH_3)SiCl + (CH_3)_3$ $COOH$ base	50	90-91/20	0.9206	1.4210	101.188
73	$(CH_2=CH)(C_2H_5)Si\left[OOC(CH_3)_3\right]_2$	$(CH_2=CH)(C_2H_5)SiCl_2$ + $+ (CH_3)_3COOH$ base	60	63/2 159 (decomp.)	0.9112	1.4241	101.188
74	$(CH_2=CH)(n\text{-}C_3H_7)Si\left[OOC(CH_3)_3\right]_2$	$(CH_2=CH)(n\text{-}C_3H_7)SiCl_2$ + $+ (CH_3)_3COOH$ base	45	76/1-1.5	0.9054	1.4269	99.101
75	$(CH_2=CH)Si(CH_3)$ $\left[OOC(CH_3)_2C_2H_5\right]_2$	$(CH_2=CH)(CH_3)SiCl_2$ + $+ t\text{-}C_5H_{11}OOH$ base		62/0.5	0.9228	1.4312	99.101
76	$(CH_2=CH)Si(n\text{-}C_3H_7)(OOC_5H_{11}\text{-}t)_2$	$(CH_2=CH)(n\text{-}C_3H_7)SiCl_2$ + $+ t\text{-}C_5H_{11}OOH$ base	66	56/0.05	0.9145	1.4359	99.101
77	$(CH_2=CH)(C_6H_5)Si\left[OOC(CH_3)_3\right]_2$	$(CH_2=CH)(C_6H_5)SiCl_2$ + adduct $(CH_3)_3COOH$ with amine	95	137 (decomp.)			70
78	$(CH_2=CH)(CH_3)Si\left[OOC(C_2H_5)_3\right]_2$	$(CH_2=CH)(CH_3)SiCl_2$ + $+ (C_2H_5)_3COOH$ base	58	62/0.5-1		1.4312	99.101
79	$(CH_2=CH)Si\left[OOC(CH_3)_3\right]_3$	$(CH_2=CH)SiCl_3 + (CH_3)_3COOH$ base	40 86	78/1 154 (decomp.)	0.9577	1.4237 1.4223	188 101 70

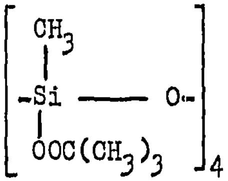
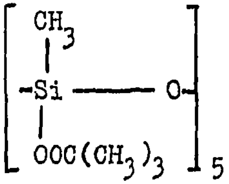
1	2	3	4	5	6	7	8	9
80	$(CH_2{=}CH)Si\left[OOC(CH_3)_2C_6H_5\right]_3$	$(CH_2{=}CH)SiCl_3$ + adduct $C_6H_5(CH_3)_2COOH$ with amine	93		140 (decomp.)			70
81	$(CH_2{=}CH{-}CH_2)(CH_3)Si\left[OOC(CH_3)_3\right]_2$	$(CH_2{=}CH{-}CH_2)(CH_3)SiCl_2$ $(CH_3)_3COOH$ base	40		31/0.1 170 (decomp.)	0.9094	1.4182	99.101
82	$(CH_2{=}CH{-}CH_2)(CH_3)_2Si$ $OOC(CH_3)_3$	$(CH_2{=}CH{-}CH_2)(CH_3)_2SiCl_2$ + + adduct $(CH_3)_3COOH$ with amine	95		178 (decomp.) 25/0.5	 0.8461	 1.4181	70 101
83	$(CH_2{=}CH{-}CH_2)Si\left[OOC(CH_3)_3\right]_3$	$(CH_2{=}CH{-}CH_2)SiCl_3$ + adduct $(CH_3)_3COOH$ with amine	80		174 (decomp.)			70
84	$H_2C{=}CHC{\equiv}CC(CH_3)_2OOSi(CH_3)_3$	$(CH_3)_3SiCl$ + $H_2C{=}CHC{\equiv}CC(CH_3)_2OOH$ base			41/1	0.8948	1.4495	120
85	$H_2C{=}C(CH_3)C{\equiv}CC(CH_3)_2OOSi$ $(CH_3)_3$	$(CH_3)_3SiCl$ + $H_2C{=}C(CH_3)C{\equiv}CC(CH_3)_2OOH$ base			56/2	0.8835	1.4485	120
86	$H_2C{=}CHC{\equiv}CC(C_2H_5)_2OOSi(CH_3)_3$	$(CH_3)_3SiCl$ + $H_2C{=}CHC{\equiv}CC(C_2H_5)_2OOH$ base			53/1	0.8882	1.4586	120
87	$H_2C{=}CHC{\equiv}CC(C_3H_7)_2OOSi(CH_3)_3$	$(CH_3)_3SiCl$ + $H_2C{=}CHC{\equiv}CC(C_3H_7)_2OOH$ base			66/1	0.8838	1.4606	120
88	$H_2C{=}C(CH_3)C{\equiv}CC(CH_3)$ $(C_2H_5)OOSi(CH_3)_3$	$(CH_3)_3SiCl$ + $H_2C{=}C(CH_3)C{\equiv}CC(CH_3)$ $(C_2H_5)OOH$ base			44/0.1	0.8884	1.4532	120

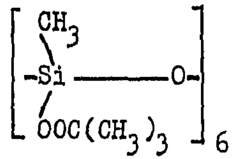
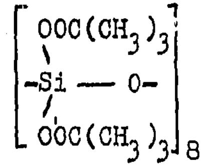
1	2	3	4	5	6	7	8	9
89	$(C_2H_5O)_3SiOOC(CH_3)_3$	$(C_2H_5O)_3SiCl + (CH_3)_3COOH$ base	66		68/1		1.3956	58.83. 33
90	$(CH_3O)_3SiOOC(CH_3)_3$	$(CH_3O)_3SiCl + (CH_3)_3COOH$ base			49/6			58.83
91	$(CH_3O)(CH_3)_2SiOOC(CH_3)_3$	$(CH_3O)(CH_3)_2SiCl + (CH_3)_3$ $COOH$ base	40		38-40/12.5	0.886	1.3959	32
		$(CH_3)_2Si[OOC(CH_3)_3]Cl +$ $+ CH_3OH$ base	45,5		42/15 35/10	0.8842 0.8878	1.3950 1.3972	114 94
92	$(C_2H_5O)(CH_3)_2SiOOC(CH_3)_3$	$(C_2H_5O)(CH_3)_2SiCl + (CH_3)_3$ $COOH$ base	76		30/2 41/10	0.874 0.8756	1.3988 1.3958	32 94
93	$(i\text{-}C_3H_7O)(CH_3)_2SiOOC(CH_3)_3$	$(i\text{-}C_3H_7O)(CH_3)_2SiCl +$ $+ (CH_3)_3COOH$ base	71		31/3	0.859	1.3971	32
		$(CH_3)_2[OOC(CH_3)_3]SiCl +$ $+ i\text{-}C_3H_7OH$ base	45		57-8/19	0.8842	1.3950	114
94	$(C_4H_9O)(CH_3)_2SiOOC(CH_3)_3$	$(C_4H_9O)(CH_3)_2SiCl + (CH_3)_3$ $COOH$ base	82		31/2 63/5	0.877	1.4063 1.4069	32 144
		$(CH_3)_2Si[OOC(CH_3)_3]Cl +$ $+ C_4H_9OH$ base	56		41-1.5/2	0.8680	1.4058	144
95	$(n\text{-}C_3H_7O)(CH_3)_2SiOOC(CH_3)_3$	$(n\text{-}C_3H_7O)(CH_3)_2SiCl + (CH_3)_3$ $COOH$ base	70		57/2	0.870	1.4018	33
96	$[(CH_3)_3CO](CH_3)_2SiOOC(CH_3)_3$	$[(CH_3)_3CO](CH_3)_2SiCl +$ $(CH_3)_3COOH$ base	60		60/13	0.857	1.4006	33

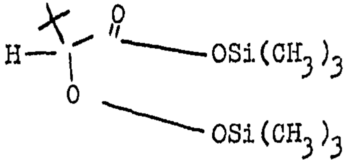
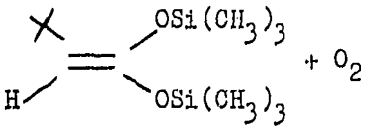
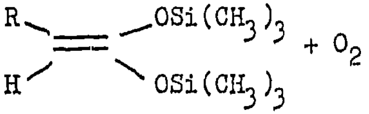
1	2	3	4	5	6	7	8	9
97	$(CH_3O)(CH_3)_2SiOOC(CH_3)_2C_6H_5$	$(CH_3O)(CH_3)_2SiCl$ + + $C_6H_5(CH_3)_2COOH$	8			-	1.4850	33
		1.4-diazobicyclooctane			60/0.7	1.0720	1.5165	94
98	$(CH_3)(C_6H_5)(CH_3O)SiOOC(CH_3)_3$	$(CH_3)(C_6H_5)(CH_3O)SiCl$ + + $(CH_3)_3COOH$ base			52/0.6	1.0031	1.4782	94
		$(CH_3)(C_6H_5)SiClOOC$ $(CH_3)_3$ + CH_3OH base	86		38/0.02	0.9921	1.4725	114
99	$(CH_3)(CH_2{=}CH)(CH_3O)SiOOC(CH_3)_3$	$(CH_2{=}CH)(CH_3O)(CH_3)SiCl$ + + $(CH_3)_3COOH$ base						94
100	$(CH_3)(CH_2Cl)(CH_3O)SiOOC(CH_3)_3$	$(CH_3)(CH_2Cl)(CH_3O)SiCl$ + + $(CH_3)_3COOH$ base						94
101	$(CH_3O)_2CH_3SiOOC(CH_3)_3$	$(CH_3O)_2CH_3SiCl$ + $(CH_3)_3COOH$ base	80		41/12	0.949	1.3940	32
102	$(CH_3O)_2CH_3SiOOC_5H_{11}$-t	$(CH_3O)_2CH_3SiCl$ + t-$C_5H_{11}OOH$ base	74		48/3	0.948	1.4029	32
103	$(C_2H_5O)CH_3SiOOC(CH_3)_3$	$(C_2H_5O)_2CH_3SiCl$ + $(CH_3)_3COOH$ base	60		43/3	0.924	1.3973	32
104	$(i\text{-}C_3H_7O)_3SiOOC(CH_3)_2C_6H_5$	$(i\text{-}C_3H_7O)_3SiCl$ + $C_6H_5(CH_3)_2$ COOH 1.4-diazobicyclooctane						33

1	2	3	4	5	6	7	8	9
105	$(CH_3O)CH_3Si[OOC(CH_3)_3]_2$	$(CH_3O)(CH_3)SiCl_2$ + + $(CH_3)_3COOH$ base	68		51/5	0.950	1.4061	32
106	$(C_2H_5O)CH_3Si[OOC(CH_3)_3]_2$	$(C_2H_5O)(CH_3)SiCl_2$ + $(CH_3)_3COOH$ base	55		38-40/1.5	0.930	1.4074	32
107	$(CH_2Cl)(CH_3)_2SiOOC(CH_3)_2C_6H_5$	$(CH_2Cl)(CH_3)_2SiCl$ + adduct $C_6H_5(CH_3)_2COOH$ with amine	95		172 (decomp.)			70
108	$CF_3CH_2CH_2Si[OOC(CH_3)_3]_3$	$CF_3CH_2CH_2SiCl_3$ + adduct $(CH_3)_3COOH$ with amine	80		177 (decomp.)			70
109	$(CH_3)_3SiC{\equiv}CC(CH_3)_2OOSi(CH_3)_3$	$(CH_3)_3SiC{\equiv}CC(CH_3)_2OOH$ + + $(CH_3)_3SiCl$ base	48		38/1	0.8810	1.4390	159
110	$C_4H_3S(CH_3)_2SiOOC(CH_3)_3$	$C_4H_3S(CH_3)_2SiCl$ + + $(CH_3)_3COOH$ base	77		59/1		1.4835	144
111	$CH_2Cl(CH_3)_2SiOOC(CH_3)_3$	$CH_2Cl(CH_3)_2SiCl$ + + $(CH_3)_3COOH$ base	70		65/20		1.4265	144
112	$C_4H_3SSi(CH_3)[OOC(CH_3)_3]_2$	$C_4H_3SSi(CH_3)Cl$ + $(CH_3)_3COOH$ base	50		$75/4 \cdot 10^{-4}$		1.4747	166
113	$C_4H_3S{-}Si[OOC(CH_3)_3]_3$	$C_4H_3SSiCl_3$ + $(CH_3)_3COOH$ base	65				1.4678	166

1	2	3	4	5	6	7	8	9
114	$CH_2=C(CH_3)CH_2O(CH_2)_3Si[OOC(CH_3)_3]_3$	$CH_2=C(CH_3)CH_2O(CH_2)_3SiCl_3+2(CH_3)_3COOH$ base	70 88		183 (decomp.) 140 (decomp.)			70 70 58.59
115	$(CH_3)_3SiOSi(CH_3)_2OO(CH_3)_3$	$(CH_3)_3SiSi(CH_3)_2Cl+LiOOC(CH_3)_3$	75	35–40		0.8602	1.3955	125
116	$(CH_3)_3COOSi(CH_3)_2OSi(CH_3)_2OSi(CH_3)_2OOC(CH_3)_3$	$(CH_3)_2Si[OSi(CH_3)_2Cl]_2 + (CH_3)_3COOH$ base	47		54/1	0.927	1.4059	32
117	$(CH_3)_3SiOOC(CH_3)_2CH_2CH_2C(CH_3)_2OOSi(CH_3)_3$	$[CH_2C(CH_3)_2OOH]_2 + (CH_3)_3SiCl$ base	81		68/1	0.889	1.4247	32
118	$(C_6H_5)_3SiOOC(CH_3)_2CH_2CH_2C(CH_3)_2OOSi(C_6H_5)_3$	$[CH_2C(CH_3)_2OOH]_2 + (C_6H_5)_3SiCl$ base	62	142–143	-	-	-	32
119	$(CH_3)_3COO[Si(CH_3)_2O]_6OC(CH_3)_3$	$ClSi(CH_3)_2\ OSi(CH_3)_2\ {}_5Cl + (CH_3)_3COOH$ base					1.4050	164
120	$(CH_3)_2[(CH_3)_3CO]SiOSi(CH_3)_2[OOC(CH_3)_3]$	$Cl(CH_3)_2SiSi(CH_3)_2Cl + (CH_3)_3COOH$ base			89–89.5/13	0.8889	1.4016	89
121	$(CH_3)_2ClSiOOC(CH_3)_3$	$(CH_3)_2SiCl_2 + (CH_3)_3COOH$ base	56		26/10. 46/20	0.959	1.4062	96
		$(CH_3)_3COOMgCl + (CH_3)_2SiCl_2$ base	43 45		49/17 44.5/20	0.947 0.962	1.4098 1.4100	33 113
122	$Cl_3SiOOC(CH_3)_3$	$SiCl_4 + (CH_3)_3COOH$ base	31		36/10	-	1.4172	33

1	2	3	4	5	6	7	8	9
123	$(CH_3)ClSi[OOC(CH_3)_3]_2$	$CH_3SiCl_3 + (CH_3)_3COOH$ base	40		45/1-2	1.0151	1.4175	96
124	$(CH_3)_2Si[OOC(CH_3)_3]NH_2$	$(CH_3)_2Si[OOC(CH_3)_3]Cl + NH_3$	54.6		38/10	0.9280	1.4120	114
125	$(C_6H_5)_2Si[OOC(CH_3)_3]NH_2$	$(C_6H_5)_2Si[OOC(CH_3)_3]Cl + NH_3$	68					114
126	$(CH_3)_2Si[OOC(CH_3)_3]$	$(CH_3)_2Si[OOC(CH_3)_3]Cl + NH_3$	71		40/0.02	0.9288	1.4245	114
127	$[(CH_3)_3COOSi(CH_3)_2]_2O$	$[Cl(CH_3)_2Si]_2O + (CH_3)_3COOH$ base	90				1.4082	162
128	$[C_6H_5(CH_3)_2COOSi(CH_3)_2]_2O$	$[Cl(CH_3)_2Si]_2O + C_6H_5(CH_3)_2$ $COOH$ base	90				1.5013	162
129	$[(CH_3)_3COOSI(C_6H_5)_2]_2O$	$[Cl(C_6H_5)_2Si]_2O + (CH_3)_3COOH$ base	80	96.4-97.5				162
130	$[C_6H_5(CH_3)_2COOSi(C_6H_5)_2]_2O$	$[Cl(C_6H_5)_2Si]_2O + C_6H_5(CH_3)_2$ $COOH$ base	70	82.3-84.2				162
131	 $\left[-\underset{OOC(CH_3)_3}{\overset{CH_3}{Si}}-O-\right]_4$	$[SiCl(CH_3)-O-]_4 + (CH_3)_3COOH$ base	85				1.4242	154
132	 $\left[-\underset{OOC(CH_3)_3}{\overset{CH_3}{Si}}-O-\right]_5$	$[-ClSi(CH_3)-O-]_5 + (CH_3)_3$ $COOH$ base	80				1.4238	154

1	2	3	4	5	6	7	8	9
133		$[-ClSi(CH_3)-O-]_6 + (CH_3)_3COOH$ base	82				1.4260	154
134		$[-Cl_2Si-O-]_8 + (CH_3)_3COOH$ base	85				1.4230	154
135	$(C_6H_5)_3SiOOCH(CCl_3)OH$	$(C_6H_5)_3SiOOH +$ $CCl_3CH(OH)(OCH_3)$	30	164-168				131
136	$Cl(C_2H_5)_2SiOOC(CH_3)_3$	$(CH_3)_3COOMgCl + (C_2H_5)_2SiCl_2$	23		69/14	0.957	1.4249	113
137	$CH_3(C_6H_5)ClSiOOC(CH_3)_3$	$(CH_3)_3COOMgCl +$ $(CH_3)(C_6H_5)SiCl_2$	45		50/0.02	1.056	1.4893	113
138	$(CH_2{=}CH)CH_3Si[OOC(CH_3)_3]Cl$	$(CH_3)_3COOMgCl +$ $(CH_2{=}CH)CH_3SiCl_2$	60		47/10	0.9773	1.4354	113
		$(CH_3)_3COOH + (CH_2{=}CH)CH_3SiCl_2$ base	58		30/2	0.9752	1.4247	96
139	$(ClCH_2)CH_3Si[OOC(CH_3)_3]Cl$	$(CH_3)_3COOMgCl +$ $(ClCH_2)CH_3SiCl_2$	64		46-47/3	1.1027	1.4350	113
140	$(CH_3)_2Si(OOC_5H_{11}\text{-}t)Cl$	$t\text{-}C_5H_{11}OOMgCl + (CH_3)_2SiCl$	47		46/11	0.9538	1.4138	113
141	$(CH_3)_3SiOOC(CH_3)_2C(O)C_6H_5$	$(CH_3)_3SiOC(C_6H_5){=}C(CH_3)_2 + O_2$						137

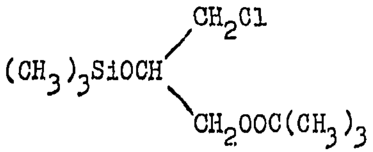
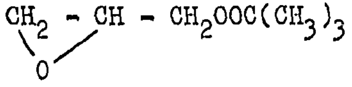
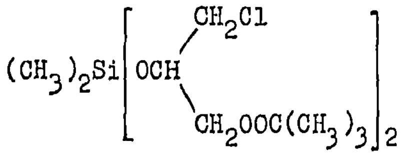
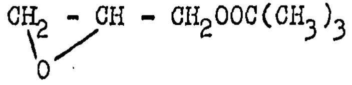
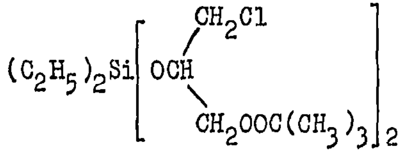
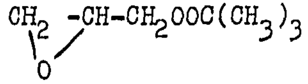
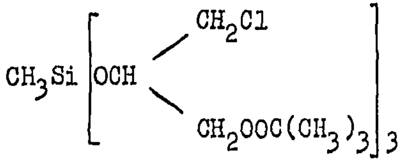
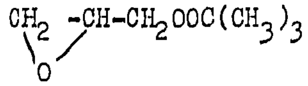
1	2	3	4	5	6	7	8	9
142					67-69/0.2			1
143	$(CH_3)_3SiOOCH(R)C(O)OSi(CH_3)_3$ R-adamanthyl							2
144	$(CH_3)_2C(CH{=}N\text{-}CH_3)OOSi(CH_3)_3$	$(CH_3)_2C{=}CHN(C_2H_5)Si(CH_3)_3+O_2$	71		47.5-9/10	0.8821	1.4235	21
145	$(CH_3)_2C(CH{=}N\text{-}C_2H_5)OOSi(CH_3)_3$	$(CH_3)_2C{=}CHN(C_2H_5)Si(CH_3)_3+O_2$	84		55-8/10	0.8865	1.427	21
146	$[(CH_3)_3SiO]_2$	$(CH_3)_3SiCl + H_2O_2$ base	43		38/30		1.3970	74
				-40÷ -39				35
		$(CH_3)_3SiCl + Na_2O_2$			36/30			139 119
		$(CH_3)_3SiCl$ + 1/2 compl. 1.4-diazobicyclo 2.2.2 octane - H_2O_2	35		42/30			49
147	$[(C_2H_5)_3SiO]_2$	$(C_2H_5)_3SiCl + H_2O_2$ base			62/0.02		1.4362	11.22 84.139
		$(C_2H_5)_3SiCl$ + complex 1.4-diazobicyclo 2.2.2 octane - H_2O_2	71		61/0.03			49
		$[(C_2H_5)_3Si]_2Hg + O_2$						122

1	2	3	4	5	6	7	8	9
148	$[(C_3H_7)_3SiO]_2$	$(C_3H_7)_3SiCl$ + complex 1.4-diazobicyclo 2.2.2 octane - H_2O_2	60		95/0.01			49
		$(C_3H_7)_3SiCl + H_2O_2$ base					1.4456	176
149	$[C_3H_7(CH_3)_2SiO]_2$	$C_3H_7(CH_3)_2SiCl$ + complex 1.4-diazobicyclo 2.2.2 octane - H_2O_2	72		81-83/10			49
150	$[n\text{-}C_4H_9(CH_3)_2SiO]_2$	$n\text{-}C_4H_9Si(CH_3)_3 + H_2SO_4 + H_2O_2$						119
151	$[(n\text{-}C_5H_{11})\ SiO]_2$	$(n\text{-}C_5H_{11})_3SiCl + H_2O_2$ base					1.4537	176
152	$[(n\text{-}C_6H_{13})_3SiO]_2$	$(n\text{-}C_6H_{13})_3SiCl + H_2O_2$						
153	$[(C_6H_5)_3SiO]_2$	$(C_6H_5)_3SiCl + H_2O_2$	53	140-141 85				54 58
			30	135-135.2				172
154	$[(C_6H_5CH_2)_3SiO]_2$	$(C_6H_5CH_2)_3SiCl + H_2O_2$ base	37	110-111				54
155	$[C_6H_5CH_3)_2SiO]_2$	$C_6H_5(CH_3)_2SiCl + H_2O_2$ base		32.5- 33.5				167 173
156	$[CH_3(C_6H_5)_2SiO]_2$	$CH_3(C_6H_5)_2SiCl + H_2O_2$ base	30	43.4- 44.1				173
157	$[(p\text{-}CH_3OC_6H_4)(CH_3)_2SiO]_2$	$(p\text{-}CH_3OC_6H_4)(CH_3)_2SiCl + H_2O_2$ base		59.5- 60.5				140.170
158	$[(p\text{-}BrC_6H_4)(CH_3)_2SiO]_2$	$(p\text{-}BrC_6H_4)(CH_3)_2SiCl + H_2O_2$ base		55-56				140.170

1	2	3	4	5	6	7	8	9
159	$[(p\text{-}CH_3C_6H_4)(CH_3)_2SiO]_2$	$(p\text{-}CH_3C_6H_4)(CH_3)_2SiCl + H_2O_2$ base	30	54.5- 56.3				140.173
160	$[(p\text{-}CH_3C_6H_4)(C_6H_5)_2SiO]_2$	$(p\text{-}CH_3C_6H_4)(C_6H_5)_2SiCl + H_2O_2$ base	70	135				138
161	$[(p\text{-}CH_3OC_6H_4)(C_6H_5)_2SiO]_2$	$(p\text{-}CH_3OC_6H_4)(C_6H_5)_2SiCl + H_2O_2$ base	64	112				138
162	$[(CH_3)_2(C_2H_5O)SiO]_2$	$(CH_3)_2(C_2H_5O)SiCl$ + 1.4-diazobicyclo- 2.2.2- octane-H_2O_2 complex			82- 84/20			49
163	$[C_6H_5CH_2(CH_3)_2SiO]_2$	$C_6H_5CH_2(CH_3)_2SiCl + H_2O_2$ base		59.5- -60.8				103
		$C_6H_5CH_2(CH_3)_2SiCl$ + 1.4-diazobicyclo 2.2.2- octane-H_2O_2 complex	45	58				49
164	$(p\text{-}BrC_6H_4)(CH_3)_2SiOOSi$- $(C_6H_5)_3$	$(n\text{-}BrC_6H_4)(CH_3)_2SiCl$ + + $(C_6H_5)_3SiOOH$	30	116- 117				169
165	$(CH_3)_3SiOOSi(C_6H_5)_3$	$(CH_3)_3SiCl + (C_6H_5)_3SiOOH$ base	70	66.5- 67				152.165
166	$(C_2H_5)_3SiOOSi(C_6H_5)_3$	$(C_2H_5)_3SiCl + (C_6H_5)_3SiOOH$ base	50	51.4- 52.5				165.168
167	$(n\text{-}C_3H_7)_3SiOOSi(C_6H_5)_3$	$(n\text{-}C_3H_7)_3SiCl + (C_6H_5)_3SiOOH$ base	50	35-36				165.168
168	$(n\text{-}C_4H_9)_3SiOSi(C_6H_5)_3$	$(n\text{-}C_4H_9)_3SiCl + (C_6H_5)_3SiOOH$ base	50	31-32				165.168

1	2	3	4	5	6	7	8	9
169	$(n\text{-}C_5H_{11})_3SiOOSi(C_6H_5)_3$	$(n\text{-}C_5H_{11})_3SiCl$ + $(C_6H_5)_3SiOOH$ base					1.5330	140.171
170	$(n\text{-}C_6H_{13})_3SiOOSi(C_6H_5)_3$	$(n\text{-}C_6H_{13})_3SiCl$ + $(C_6H_5)_3SiOOH$ base					1.5245	140.171
171	$n\text{-}C_4H_9(CH_3)_2SiOOSi(C_6H_5)_3$	$n\text{-}C_4H_9(CH_3)_2SiCl$ + $(C_6H_5)_3SiOOH$ base	35				1.5560	169
172	$C_6H_5(CH_3)_2SiOOSi(C_6H_5)_3$	$C_6H_5(CH_3)_2SiCl$ + $(C_6H_5)_3SiOOH$ base		80- 80.5				165.167
173	$CH_3(C_6H_5)_2SiOOSi(C_6H_5)_3$	$CH_3(C_6H_5)_2SiCl$ + $(C_6H_3)_3SiOOH$						172
174	$C_6H_5CH_2(CH_3)_2SiOOSi(C_6H_5)_3$	$C_6H_5CH_2(CH_3)_2SiCl$ + $(C_6H_5)_3SiOOH$ base					1.5812	
175	$(p\text{-}CH_3C_6H_4)(CH_3)_2SiOOSi(C_6H_5)_3$	$(p\text{-}CH_3C_6H_4)(CH_3)_2SiCl$ + $(C_6H_5)_3SiOOH$	50	77.4- 78.3				169
176	$(p\text{-}CH_3OC_6H_4)(CH_3)_2SiOOSi(C_6H_5)_3$	$(p\text{-}CH_3OC_6H_4)(CH_3)_2SiCl$ + $(C_6H_5)_3SiOOH$ base	20	36- 37.5				169
177	$(CH_3)_3SiOOGe(C_6H_5)_3$	$(CH_3)_3SiCl$ + $(C_6H_5)_3GeOOH$ base	70- 80	59- 60				152.180

1	2	3	4	5	6	7	8	9
178	$(C_2H_5)_3SiOOGe(C_6H_5)_3$	$(C_2H_5)_3SiCl + (C_6H_5)_3GeOOH$ base	70	40- 41				165.182
179	$(C_3H_7\text{-}n)_3SiOOGe(C_6H_5)_3$	$(n\text{-}C_3H_7)_3SiCl + (C_6H_5)_3GeOOH$ base	60	35.2- 36.2				182
180	$(n\text{-}C_4H_9)_3SiOOGe(C_6H_5)_3$	$(n\text{-}C_4H_9)_3SiCl + (C_6H_5)_3GeOOH$ base	48	31- 32				165.182
181	$(n\text{-}C_5H_{11})_3SiOOGe(C_6H_5)_3$	$(n\text{-}C_5H_{11})_3SiCl + (C_6H_5)_3GeOOH$ base	50				1.5299	182
182	$(CH_3)_2C_6H_5SiOOGe(C_6H_5)_3$	$C_6H_5(CH_3)_2SiCl + (C_6H_5)_3GeOOH$ base						165.180
183	$(C_6H_5)_3SiOOGe(C_6H_5)_3$	$(C_6H_5)_3SiCl + (C_6H_5)_3GeOOH$ base	85	142- 142.5				138.152. 165
184	$(C_6H_5)_3SiOOSb(C_6H_5)_4$	$(C_6H_5)_4Sb + (C_6H_5)_3SiOOH$ base	70 90	105- 108				135
185	$\left[(C_6H_5)_3SiOO\right]_2Sb(C_6H_5)_3$	$(C_6H_5)_3SbCl_2 + (C_6H_5)_3SiOOH$ base	82		120 (decomp.)			128
186	$(CH_3)_3SiOOSO_2OSi(CH_3)_3$	$(CH_3)_3SiOOSI(CH_3)_3 + SO_3$	100	-11. -12				35
187	$(CH_3)_3SiC\equiv CC(CH_3)_2OOH$	$(CH_3)_3SiC\equiv CC(CH_3)_2OH + H_2O_2 + H_2SO_4$	60		53.1	0.9183	1.4448	159
188	$(CH_3)_3SiC\equiv CC(CH_3)_2OOC(CH_3)_3$	$(CH_3)_3SiC\equiv CC(CH_3)_2OH + (CH_3)_3COOH + H_2SO_4$	60		54/2	0.8412	1.4264	159
189	$(CH_3)_3SiC\equiv CC(CH_3)_2OOC(CH_3)_2C_2H_5$	$(CH_3)_3SiC\equiv CC(CH_3)_2OH + C_2H_5(CH_3)_2COOH + H_2SO_4$	55		43/1	0.8386	1.4296	159

1	2	3	4	5	6	7	8	9
190	$(CH_3)_3SiC\equiv CC(CH_3)_2OOC$ $(CH_3)_2C\equiv CH$	$(CH_3)_3SiC=CC(CH_3)_2OH$ $+ HC=C(CH_3)_2COOH + H_2SO_4$	60		45/0.8	0.8767	1.4438	159
191	$(CH_3)_3SiC\equiv CC(CH_3)_2OOC$ $(CH_3)_2C\equiv C-CH=CH_2$	$(CH_3)_3SiC=CC(CH_3)_2OOH$ $+ CH_2=CH-C=C(CH_3)_2COH + H_2SO_4$	32			0.8834	1.4652	159
192	$(CH_3)_3SiC\equiv CC(CH_3)_2OOC$ $(CH_3)_2C\equiv C-Si(CH_3)_3$	$(CH_3)_3SiC=CC(CH_3)_2OOH +$ $(CH_3)_3SiC=CC(CH_3)_2OH + H_2SO_4$	73	25				159
193		 $+ (CH_3)_3SiCl$				0.9557	1.43	187
194		 $+ (CH_3)_2SiCl_2$	81.8			1.0625	1.4405	187
195		 $+ (C_2H_5)_2SiCl_2$	73			0.0520	1.4460	187
196		 $+ CH_3SiCl_3$	98			1.1130	1.4518	187

1	2	3	4	5	6	7	8	9
197	$(CH_3)_3SiCH_2CH_2C(O)OOC(CH_3)_3$	$(CH_3)_3SiCH_2CH_2C(O)Cl$ + + $NaOOC(CH_3)_3$	60		59-60/0.5	1.9085	1.4312	160
198	$(CH_3)_3Si(CH_2)_3C(O)OOC(CH_3)_3$	$(CH_3)_3Si(CH_2)_3C(O)Cl$ + + $LiOOC(CH_3)_3$				0.8986	1.4311	124
199	$(CH_3)_2C_6H_5Si(CH_2)_3C(O)OOC(CH_3)_3$	$(CH_3)_2C_6H_5Si(CH_2)_3C(O)Cl$ + + $LiOOC(CH_3)_3$				0.9829	1.4933	124
200	$(CH_3)_3Si(CH_2)_3C(O)OOC(CH_3)_2C_6H_5$	$(CH_3)_3Si(CH_2)_3C(O)Cl$ + + $LiOOC(CH_3)_2C_6H_5$				0.9691	1.4853	124
201	$(CH_3)_2C_6H_5Si(CH_2)_3C(O)OOC(CH_3)_2C_6H_5$	$(CH_3)_2C_6H_5Si(CH_2)_3C(O)Cl$ + + $LiOOC(CH_3)_2C_6H_5$				1.0256	1.5229	124
202	$(CH_3)_3SiCH_2CH(CH_3)C(O)OOC(CH_3)_3$	$(CH_3)_3SiCH_2CH(CH_3)C(O)Cl$ + + $LiOOC(CH_3)_3$	85			0.8882	1.4272	123
203	$(CH_3)_3Si(CH_2)_2C(O)OOC(CH_3)_2C_6H_5$	$(CH_3)_3Si(CH_2)_2C(O)Cl$ + + $NaOOC(CH_3)_2C_6H_5$	80			0.988	1.4865	39
204	$(CH_3)_3SiCH_2CH_2C(O)O_2$	$(CH_3)_3SiCH_2CH_2C(O)Cl$ + H_2O_2 base	35	30				40
205	$(C_2H_5)_3SiCH_2C(O)OOC(CH_3)_3$	$(C_2H_5)_3SiCH_2C(O)Cl$ + + $LiOOC(CH_3)_3$	60		73/1.5	0.9191	1.4495	40
206	$(CH_3)_2C_6H_5SiCH_2CH_2C(O)OOC(CH_3)_3$	$(CH_3)_2C_6H_5SiCH_2CH_2C(O)Cl$ + + $LiOOC(CH_3)_3$	70			0.9874	1.4922	37
207	$(CH_3)_2C_6H_5SiCH_2CH_2C(O)OOC(CH_3)_2C_6H_5$	$(CH_3)_2C_6H_5SiCH_2CH_2C(O)Cl$ + + $LiOOC(CH_3)_2C_6H_5$	75			1.0430	1.5226	37

1	2	3	4	5	6	7	8	9
208	$(CH_3)_3SiOCH_2OOC(CH_3)_3$	$(CH_3)_3SiCl + (CH_3)_3COOCH_2OH$ base	77			0.8788	1.4045	20
209	$CH_3Si[OCH_2OOC(CH_3)_3]_3$	$CH_3SiCl_3 + (CH_3)_3COOCH_2OH$ base				1.0113	1.4225	20
210	$CH_3(CH_2{=}CH)Si[OCH_2OOC(CH_3)_3]_2$	$CH_3(CH_2{=}CH)SiCl_2 + (CH_3)_3COOCH_2OH$ base				0.9779	1.4300	20
211	$(CH_3)_3SiOCH_2C(O)OOC(CH_3)_3$	$(CH_3)_3SiCl + HOCH_2C(O)OOC(CH_3)_3$ base	79.5			0.8812	1.4050	191
212	$(C_2H_5)_3SiOCH_2C(O)OOC(CH_3)_3$	$(C_2H_5)_3SiCl + HOCH_2C(O)OOC(CH_3)_3$ base	78			0.8862	1.4230	191
213	$(CH_3)_2Si[OCH_2C(O)OOC(CH_3)_3]_2$	$(CH_3)_2SiCl_2 + HOCH_2C(O)OOC(CH_3)_3$ base	72			0.9712	1.4150	191
214	$CH_3(CH_2{=}CH)Si[OCH_2C(O)OOC(CH_3)_3]_2$	$CH_3(CH_2{=}CH)SiCl_2 + HOCH_2C(O)OOC(CH_3)_3$ base	74			0.9822	1.4240	191
215	$C_6H_5Si[OCH_2C(O)OOC(CH_3)_3]_3$	$C_6H_5SiCl_3 + HOCH_2C(O)OOC(CH_3)_3$ base	82			1.0412	1.4580	191
216	$Si[OCH_2C(O)OOC(CH_3)_3]_4$	$SiCl_4 + HOCH_2C(O)OOC(CH_3)_3$ base	87			1.0102	1.4210	191
217	$(CH_3)_3C[OSi(CH_3)_2]_2OOC(CH_3)_3$	$(CH_3)_3C[OSi(CH_3)_2]_2Cl + HOOC(CH_3)_3$ base			62/6		1.4022	192

1	2	3	4	5 6	7	8	9
218	$(CH_3)_3C[OSi(CH_3)_2]_3OOC(CH_3)_3$	$(CH_3)_3C[OSi(CH_3)_2]_3Cl$ + + $HOOC(CH_3)_3$ base			0.9101	1.4040	192
219	$(CH_3)_3COSi(CH_3)_2OOC(CH_3)_2C_6H_5$	$(CH_3)_3COSi(CH_3)_2Cl$ + + $HOOC(CH_3)_2C_6H_5$ base			0.9709	1.4675	192
220	$(CH_3)_3C[OSi(CH_3)_2]_2OOC(CH_3)_2C_6H_5$	$(CH_3)_3C[OSi(CH_3)_2]_2Cl$ + + $HOOC(CH_3)_2C_6H_5$ base			0.9665	1.4530	192
221	$(CH_3)_3C[OSi(CH_3)_2]_3OOC(CH_3)_2C_6H_5$	$(CH_3)_3C[OSi(CH_3)_2]_3Cl$ + + $HOOC(CH_3)_2C_6H_5$ base			0.9641	1.4430	192
222	$C_6H_5OSi(CH_3)_2OOC(CH_3)_3$	$C_6H_5OSi(CH_3)_2Cl$ + $HOOC(CH_3)_3$ base		31/0.05	0.9940	1.4745	192
223	$C_6H_5OSi(CH_3)_2OOC(CH_3)_2C_6H_5$	$C_6H_5OSi(CH_3)_2Cl$ + $HOOC(CH_3)_2C_6H_5$ base			1.0400	1.5106	192
224	$[(CH_3)_3SiO](CH_3)_2SiOOC(CH_3)_3$	$[(CH_3)_3SiO](CH_3)_2SiCl$ + + $(CH_3)_3COOH$ base	62	46–52/0.5	0.8613	1.4041 1.3952	193 192
225	$[(CH_3)_3SiO]_2(CH_3)SiOOC(CH_3)_3$	$[(CH_3)_3SiO]_2(CH_3)SiCl$ + + $(CH_3)_3COOH$ base	56	69/0.5 90/20	0.8812	1.3980 1.3951	193 192
226	$[(CH_3)_3SiO]_3SiOOC(CH_3)_3$	$[(CH_3)_3SiO]_3SiCl$ + $(CH_3)_3COOH$ base	50	65–69/0.1 96/2.5	0.8921	1.3973 1.3957	193 192

1	2	3	4	5	6	7	8	9
227	$C_6H_5(CH_3)_2SiOSi(CH_3)_2OOC(CH_3)_3$	$C_6H_5(CH_3)_2SiOSi(CH_3)_2Cl$ + $HOOC(CH_3)_3$ base			98/0.05	0.9522	1.4610	192
228	$[C_6H_5(CH_3)_2SiO]_2(CH_3)SiOOC(CH_3)_3$	$[C_6H_5(CH_3)_2SiO]_2(CH_3)SiCl$ + $HOOC(CH_3)_3$ base				1.0090	1.4900	192
229	$(CH_3)_3COOSi(CH_3)_2OOC(CH_3)_2C_6H_5$	$(CH_3)_3COOSi(CH_3)_2Cl$ + $HOOC(CH_3)_2C_6H_5$ base				1.0020	1.4717	192
230	$(CH_3)_3COO(CH_3)_2SiOSi(CH_3)_2Cl$	$Cl(CH_3)_2SiOSi(CH_3)_2Cl$ + $HOOC(CH_3)_3$ base	60		67/10	0.9609	1.4070	192
231	$(CH_3)_3COO(CH_3)_2SiOSi(CH_3)_2OSi(CH_3)_2Cl$	$Cl(CH_3)_2SiOSi(CH_3)_2OSi(CH_3)_2Cl$ + $HOOC(CH_3)_3$ base			78/5	0.9601	1.4061	192
232	$[C_4H_9OOSi(CH_3)(CH{=}CH_2)OSi(CH_3)_2]_2O$	$C_4H_9OOSi(CH_3)(CH{=}CH_2)Cl$ + $HO[Si(CH_3)_2O]_2H$ base	92			0.9465	1.4186	194
233	$(CH_3)_2\overline{C(CH_2)_2C(CH_3)_2OOSi(CH_3)_2OO}$	$(CH_3)_2C(OOH)(CH_2)_2C(CH_3)_2OOH$ + $(CH_3)_2SiCl_2$ base	62.4	44.5-8				195
234	$(CH_3)_3SiOOC_6H_{10}OOC_6H_{10}OOSi(CH_3)_3$	$(HOOC_6H_{10}O)_2$+ $(CH_3)_3SiCl$ base		63.5-64.5				196
235	$CH_3(C_2H_5)(H)SiOOC(CH_3)_3$	$CH_3(C_2H_5)(H)SiCl$ + $NaOOC(CH_3)_3$						197

1	2	3	4	5	6	7	8	9
236	$CH_3(C_2H_5)(H)SiOOC(CH_3)_3$	$CH_3(C_6H_5)(H)SiCl + NaOOC(CH_3)_3$						197
237	$CH_3(C_6H_5)(H)SiOOC(CH_3)_2C_6H_5$	$CH_3(C_6H_5)(H)SiCl + NaOOC(CH_3)_2C_6H_5$						197
238	$CH_3(C_2H_5)(H)SiOOC(CH_3)_2C_6H_5$	$CH_3(C_2H_5)(H)SiCl + NaOOC(CH_3)_2C_6H_5$						197
239	$(C_6H_5)_2(H)SiOOC(CH_3)_3$	$(C_6H_5)_2(H)SiCl + NaOOC(CH_3)_3$						197
240	$(C_2H_5)_2(H)SiOOC(CH_3)_3$	$(C_2H_5)_2(H)SiCl + NaOOC(CH_3)_3$						197

The high selectivity of this reaction should be mentioned. This allows the synthesis of organosilicon peroxides to be conducted with retention of various and complex substituents on silicon atom (Table 1, comp. 48-51, 66-83, 89-114).

The reaction of $R_{4-n}SiCl_n$ with R'OOH proceeds with consecutive substitution of chlorine on the Si atom by R'OOH groups. This makes possible the partial displacement of chlorine on silicon atom by R'OO-groups (Table 1, comp. 121-123).

In organic solvents the organosilicon halides react with ammonia: X = halogen

$$R_{4-(n+m)}Y_mSiX_n + NH_3 \rightleftharpoons R_{4-(n+m)}Y_mSiX_{n-1}NH_2 + HX \qquad 1.5$$

$$R_{4-(n+m)}SiY_mX_{n-1}NH_2 + R_{4-(n+m)}Y_mSiX_n \rightleftharpoons$$

$$\rightleftharpoons R_{4-(n+m)}Y_mSiX_{n-1}NHX_{n-1}SiY_mR_{4-(n+m)} + HX \qquad 1.6$$

and so on.

Reactions 1.5 and 1.6 form the basis for synthesis of $(CH_3)_2$-$Si[OOC(CH_3)_3]NH_2$, $(C_6H_5)_2Si[OOC(CH_3)_3]NH_2$ and $(CH_3)_2Si[OOC(CH_3)_3]$-$NHSi[OOC(CH_3)_3](CH_3)_2$ (Table 1, comp. 124-126).

Trialkylsilyl-substituted amines, in turn, react with organic hydroperoxides with formation of organosilicon peroxides (Table 1, comp. 8, 14, 52).

$$(CH_3)_3SiNHR + (CH_3)_3COOH \rightleftharpoons (CH_3)_3SiOOC(CH_3)_3 + NH_2R \qquad 1.7$$

$$(CH_3)_3SiN(CH_3)_2 + ROOH \rightleftharpoons (CH_3)_3SiOOR + NH(CH_3)_2 \qquad 1.8$$

Organic acids are used to remove the amines.

It should be noted that alkali metal salts of organic hydroperoxides (R'OOM) react irreversibly with $R_{4-n}SiCl_n$ in hydrocarbon medium:

$$R_{4-n}SiCl_n + R'OOM \longrightarrow R_{4-n}Si(OOR')_n + nMCl \qquad 1.9$$

In this case no additives are required in order to drive the reaction to completion. This procedure was useful for syntheses of some organosilicon peroxides (Table 1, comp. 115).

Organosiloxane peroxides including polysiloxanes with organosilicon peroxide substituents have been prepared:

$$[-R_2XSiO-]_n + nR'OOH \rightleftharpoons [-R_2(R'OO)SiO-]_n + nHX \qquad 1.10$$

(Table 1, comp. 127–134).
In this case a base also is used for trapping the hydrogen halide.

Syntheses via organosilicon hydroperoxides. Organosilicon hydroperoxides can react with high selectivity with the ether function of hemiacetols. For example:

$$(C_6H_5)_3SiOOH+Cl_3CCH(OH)OCH_3 \longrightarrow (C_6H_5)_3SiOO(Cl_3C)CH(OH)+CH_3OH \qquad 1.11$$

This reaction served as the basis for another organosilicon peroxide syntheses. (Table 1, comp. 135).

Syntheses via organomagnesium compounds. The reaction of R'OOMgCl with organosilicon chlorides is the basis of the yet another method of organosilicon peroxide syntheses. The reaction is carried out in organic solvents at room temperature or below.

$$xR'OOMgCl + R_{4-n}SiCl_n \longrightarrow R_{4-n}Si(OOR')_xCl_{n-x} + xMgCl_2 \qquad 1.12$$

(Table 1, comp. 121, 136–140).

Syntheses by reactions of organosilicon compounds with oxygen and ozone. The oxidation of some complex organosilicon compounds with oxygen results in organosilicon peroxides in quantitative yield. Thus, $RR'C = CHN(R'')SiMe_3$ reacts with oxygen in the air, in water or a polar organic solvent at room temperature:

$$RR'C = CHN(R'')Si(CH_3)_3 + O_2 \longrightarrow RR'C = CHN(R'')OOSi(CH_3)_3 \qquad 1.13$$

(Table 1, comp. 141–145).

ORGANOSILICON PEROXIDES WITH SiOOSi AND SiOOE LINKAGES

The general method of synthesis of peroxides of the SiOOSi Type involves the reaction of an organosilicon chloride with hydrogen peroxide in the presence of compounds which bind the hydrogen chloride evolved.

$$2R_3SiCl + H_2O_2 \rightleftharpoons R_3SiOOSiR_3 + 2HCl \qquad 1.14$$

A substantial number of organosilicon peroxides with the SiOOSi linkage was obtained in this way (Table 1, comp. 146-164). Alkali metal peroxides may be used instead of hydrogen peroxide (Table 1, comp. 146).

Reaction 1.14 proceeds by way of intermediate organosilicon hydroperoxides (1.1). The organosilicon hydroperoxide then reacts with the organosilicon chloride:

$$R_3SiOOH + R_3SiCl \rightleftharpoons R_3SiOOSiR_3 + HCl \qquad 1.15$$

Unsymmetrical bis(silyl)peroxides may be prepared by this method. (Table 1, comp. 165-176):

$$R_3SiOOH + R'_3SiCl \rightleftharpoons R_3SiOOSiR'_3 + HCl \qquad 1.16$$

Reaction 1.16 also proceeds readily when an organogermanium hydroperoxide is used. (Table 1, comp. 177-183):

$$R_3GeOOH + R'_3SiCl \rightleftharpoons R_3GeOOSiR'_3 + HCl \qquad 1.17$$

or when chlorides of other elements are used.

Thus, the syntheses of peroxides with the SiOOSb system have been prepared (Table 1, comp. 184-185):

$$Ph_3SiOOH + Ph_4SbCl \rightleftharpoons Ph_3SiOOSbPh_4 + HCl \qquad 1.18$$

Organosilicon peroxides with SiOOSi linkages can be obtained with quantitative yield by oxidation of $(Et_3Si)_2Hg$ with oxygen in the presence of catalytic quantities of organic bases (L):

$$(Et_3Si)_2Hg + O_2 \xrightarrow{(L)} Et_3SiOOSiEt_3 + Hg \qquad 1.19$$

The reaction is conducted in hydrocarbon solution below room temperature. (Table 1, comp. 146).

Peroxides with the SiOOS linkage also have been described (35). Their synthesis proceeds by way of the reaction of SO_3 with bis-(trimethylsilyl)peroxide

$$(CH_3)_3SiOOSi(CH_3)_3 + SO_3 \longrightarrow (CH_3)_3SiOOSO_2OSi(CH_3)_3 \qquad 1.20$$

(Table 1, comp. 186).

ORGANOSILICON PEROXIDES WITH THE PEROXIDE FUNCTION IN THE γ-POSITION RELATIVE TO SILICON

The synthesis of more complex organosilicon peroxides have been described:

$$(CH_3)_3SiC{\equiv}C(CH_3)_2COH + H_2O_2 \xrightarrow{H_2SO_4} (CH_3)_3SiC{\equiv}C(CH_3)_2COOH \qquad 1.21$$

$$(CH_3)_3SiC{\equiv}CC(CH_3)_2OH + ROOH \xrightarrow{H_2SO_4} (CH_3)_3SiC{\equiv}CC(CH_3)_2OOR + H_2O \quad 1.22$$

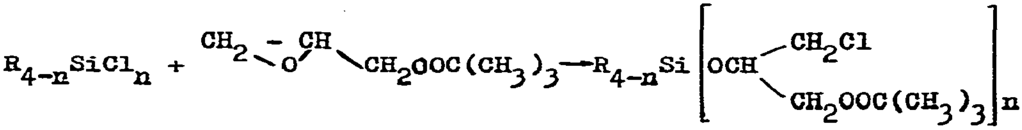
Where $R=(CH_3)_3C$, $C_6H_5(CH_3)_2C$, $HC{\equiv}C(CH_3)_2C$, $(CH_3)_3SiC{\equiv}C(CH_3)_2C$

as well as:

$$(CH_3)_3SiC{\equiv}C(CH_3)_2COOH + CH_2 = CH - C{\equiv}C(CH_3)_2COH \xrightarrow{H_2SO_4}$$
$$\longrightarrow (CH_3)_3SiC{\equiv}C(CH_3)_2COOC(CH_3)_2C{\equiv}C{-}CH{=}CH_2 + H_2O \qquad 1.23$$

(Table 1, comp. 187-192).

Another procedure for the syntheses of organosilicon peroxide with the peroxide function in the γ-position utilizes the known reaction of organosilicon chlorides with peroxide derivatives of epoxy compounds:



1.24

$$R_{4-n}SiCl_n + \underset{\diagdown O \diagup}{CH_2 - CH}{\diagdown}CH_2OOC(CH_3)_3 \longrightarrow R_{4-n}Si\left[OCH\begin{matrix}\diagup CH_2Cl\\ \diagdown CH_2OOC(CH_3)_3\end{matrix}\right]_n \qquad 1.24$$

where n= 1,2,3 (Table 1, comp.).

PHYSICAL PROPERTIES

Under normal conditions organosilicon hydroperoxides, Alk_3SiOOH, are liquids. The replacement of the alkyl groups on silicon by aryl groups results in solids. As the number of aryl groups on silicon increases the melting points of the peroxides increase. This is the case also for organosilicon peroxides. For peroxides $Alk_{4-n}Si(OOAlk')_n$, as n increases the melting point increases (for example, $[Si\ OOC(CH_3)_3]_4$ is a crystalline solid.)

The $Me_3SiOOSiMe_3$ structure has been studied by gas phase electron diffraction (87). The following interatomic distances (A°) and angles were found: O - O, 1.481; Si - O, 1.681; Si - C, 1.855; $\sphericalangle$SiOO, 106.6°; (SiOOSi) 143.5°.

For hexamethylcyclotrisilaperoxane, $[-Si(Me_2)_2OO-]_3$, (a crystalline solid under normal conditions) the following of internuclear distances (A°) and angles have been found: O - O, 1.492; Si - O, 1.674; Si - O, 1.833; $\sphericalangle$SiOO, 104.9°; δ (SiOOSi), 135.0°.

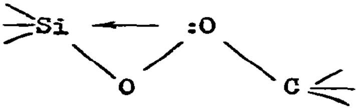
Analysis of the geometrical parameters of these organosilicon compounds showed a significant weakening of the Si - O bond in comparison to the siloxane bond (for Si -O r_a is not more than 1.65 A° (28)) and a small change of the O -O bond distance compared to hydrogen peroxide (r_a= 1.472 - 1.483 A°(73)).

The dissociation energy of the O-O bond in trimethyl(tert-butylperoxy)silane(121) is 47 kcal/mol, some 10 kcal/mol more than the dissociation energy of the O - O bond in dialkyl peroxides, 37-39 kcal/mol (51, 92).

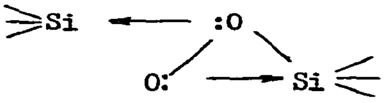
An infrared spectroscopic study of the acidity of the hydroperoxides, $(C_6H_5)_3MOOH$, where M=C,Si,Ge,Sn(61), showed that the effective electronegativity falls in the following sequence: $Si > Ge > C > Sn$, indicating a partial π-character of the bonds between the Si-subgroup elements and oxygen.

The organosilicon peroxides show characteristic absorption bands of the O -O bond in the 890-940 cm^{-1} range (70, 140, 165). The frequency and intensity of the bands increase with the number of the peroxy groups on the Si-atom (70). The IR-spectra of group 4 organoelement peroxides make possible studies of the electronic effects of organoelement substituents. It was found that $(p-d)\pi$- interaction is much stronger in the Si - O bond than in the Ge -O bond (91,141).

For organosilicon peroxides in the electronic ground state the intramolecular coordination between oxygen and silicon was proposed to be of the following types (90):



and



All the organosilicon peroxides are monomeric, covalent compounds, which are soluble in ether, benzene, chloroform and other organic solvents. However, the solubility in normal hydrocarbons is limited. An interaction of the specific solvation type is observed between organosilicon peroxides and some organic compounds(7,18). As this takes place, some organic solvents (olefins, pyridines, amines and others) act as electron donors toward the peroxide due to coordination at silicon, while other solvents (proton donors such as chloroform, phenylacetylene and others) show typical hydrogen bonding, acting as electron - acceptors toward the α- oxygen atom of the peroxide group.

CHEMICAL PROPERTIES

Thermal decomposition

Organosilicon hydroperoxides, R_3SiOOH. Thermal decomposition of hydroperoxides proceeds at a measurable rate above 100°C (Table 2, comp. 1-4). The formation of the appropriate dioxy-derivatives is the major decomposition process.

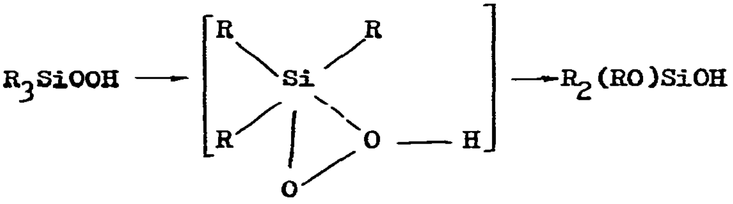
$$R_3SiOOH \longrightarrow R_2Si(OR)OH \qquad 3.1$$

An investigation of the dependence of the reaction mechanism on the reaction conditions gave indication of both homolytic and heterolytic decomposition processes.

The insensitivity to changes in the polarity of the medium, the accelerating action of UV-irradiation and the absence of acid catalysis point to a homolytic mechanism of the reaction (53, 55):

$$R_3SiOOH \longrightarrow R_3SiO^\bullet + HO^\bullet \qquad 3.2$$
$$R_3SiO^\bullet \longrightarrow R_2(RO)Si^\bullet \qquad 3.3$$
$$R_2(RO)Si^\bullet + HO^\bullet \longrightarrow R_2(RO)SiOH \qquad 3.4$$
$$R^\bullet + R_3SiOOH \longrightarrow RH + R_3SiOO^\bullet \qquad 3.5$$
$$2R_3SiOO^\bullet \longrightarrow 2R_3SiO^\bullet + O_2 \qquad 3.6$$

A heterolytic route should be facilitated by d -bonding of silicon with the β-oxygen of the peroxide group. Rearrangement of the hydroperoxide would then occur as shown below (179):



3.7

It should be noted (74) that the hydroperoxides of the Si-subgroup elements can disproportionate:

$$2R_3EOOH \longrightarrow R_3EOOER_3 + H_2O_2 \qquad 3.8$$

Reaction 3.8 may be accompanied by the formation of the perhydrate of the initial hydroperoxide, as was found in the case of organotin hydroperoxides(12).

Organosilicon peroxides, $R_{4-n}Si(OOR)_n$. Peroxides of this type are thermally stable in inert solvents (Table 2) and they are more stable than analogous peroxides of other elements of silicon subgroup.

The thermal stability of $Alk_3SiOOCAlk'_3$ -type peroxides decreases when CH_3 on Si is replaced by other alkyl substituents (Table 2, comp. 5, 14) or when the alkyl groups on silicon or carbon are replaced by aryl groups (Table 2, comp. 5-8, 22-25) or when an aryl group on silicon is replaced by SiR_3. For peroxides of type Et(Me)$(CH_2{=}CH)SiOOCMe_2R$ the thermal stability decreases in the following sequence: Me > Ph > Et (Table 2, comp. 30-32).

Compared to that of $R_3SiOOCR_3$, the thermal stability of the peroxides with a siloxane bond is significantly higher: $(R'_3COOSiR_2)_2O$ or $[-Si(OOCR'_3)R-O-]_n$ (Table 2, comp. 5 and 42, 47-49). For polyperoxides, $R_{4-n}Si(OOCR'_3)_n$, the thermal stability decreases with increasing n (Table 2, comp. 5, 26-28).

The results of various investigators suggest that thermal decomposition of organosilicon peroxides (depending on their nature and environment) may proceed via different mechanisms:

homolytic decomposition:

$$R_3SiOOCR'_3 \longrightarrow R_3SiO^{\bullet} + R'_3CO^{\bullet} \qquad 3.9$$

heterolytic rearrangement:

$R_3SiOOCR'_3 \longrightarrow R_2(RO)SiOCR'_3$ 3.10

$R_3SiOOC(H)R'_2 \longrightarrow R_3SiOH + R'_2CO$ 3.11

$R_2HSiOOCR'_3 \longrightarrow R_2SiO + R'_3COH$ 3.12

In a hydrogen atom donor solvent, the following free radical process occurs after eq. 3.9

(Continued on p. 48)

TABLE 2

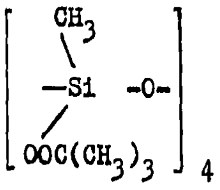
Thermal decomposition of organosilicon peroxides

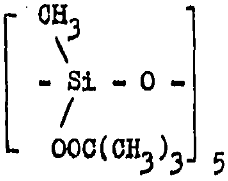
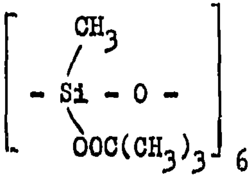
Nº	Peroxide	Solvent	Concentration mol/l	Decomp. interval, C°	T°C	$k.10^5$ sec^{-1}	$\lg k_o$	E_{act} $\frac{kcal}{mol}$	Ref.
1	2	3	4	5	6	7	8	9	10
1	$(C_6H_5)_3SiOOH$	anisole	0.05	128-154	128	10.9		22.63	55
		methylbenzoate	0.05	128-154	128	12.3		26.95	55
		nitrobenzene	0.05	128-154	128	7.6		27.63	55
		o-dichlorobenzene	0.05	132-154	132	10		27.10	55
2	$(C_6H_5)_2CH_3SiOOH$	o-dichlorobenzene	0.03	118-150	118	1.41		26.64	55
3	$(C_6H_5CH_2)_3SiOOH$	o-dichlorobenzene	0.03	118-138	118	6.37		26.40	55
4	$(C_6H_{13})_3SiOOH$	o-dichlorobenzene	0.05		130	6.27			55
5	$(CH_3)_3SiOOC(CH_3)_3$	n-heptane	0.141	180-200	183.5	2.78		41.2	81
		isooctane	0.141	180-200	183.6	2.64		41.2	81
		tetralin	0.156	180-200	193.9	15.0			81
		tert-butylbenzene	0.156	180-200	192.8	10.9			81
		1-octane	0.143	180-200	183.4	2.85		42.3	81
		dimethylphtalate	0.04		190	6.10	14.45	39.5	158
		tetradecane	0.04		190	4.80	14.44	39.7	158
		isopropylbenzene	0.02	120-140	140	0.038	15.11	40.7	101
		chlorobenzene	0.04	190-220	190	12.00	14.06	38.0	158
			0.05		190	13.0		38.0	190
		n-decane	0.05		200	11.7			16
			0.2						16
			0.57						16

1	2	3	4	5	6	7	8	9	10
		anisole	0.05	180-210	180	4.1	13.9	37.9	185
		n-nonane	0.05	180-210	180	1.9	13.5	37.9	185
			0.02	170-210	190	5.1	14.5	41.1	6.7
		styrene	0.2	170-210	190	5.9	14.8	40.2	7
		heptene-1	0.2	170-210	190	4.5	14.0	38.8	6.7
		α-methylstyrene	0.2	170-210	190	6.2	13.1	36.6	6.7
		triisobutylene	0.2	170-210	190	7.0	9.0	27.9	7
		cyclohexene	0.2	170-210	190	8.4	10.0	31.7	6.7
		1.1-diphenylethylene	0.2	170-210	190	14.1	9.9	29.1	6.7
		anethole	0.2	170-210	190	14.5	9.8	29.1	7
		gas phase	0.01	180-210	180	3.56	11.3	32.7	163
6	$(CH_3)_3SiOOC(CH_3)_2C_6H_5$	anisole	0.05	180-210	180	5.7	14.3	38.4	185
		isopropylbenzene	0.05	180-210	180	3.0	16.2	43	185
		n-nonane	0.05	180-210	180	2.5	15.2	41.2	185
7	$(CH_3)_3SiOOC(C_6H_5)_2CH_3$	anisole	0.05	170-210	180	9.8	14.6	38.6	185
		isopropylbenzene	0.05	170-200	180	7.2	15.4	40.6	185
		n-nonane	0.05	170-200	180	5.8	14.5	39	185
8	$(CH_3)_3SiOOC(C_6H_5)_3$	anisole	0.05	160-190	180	31.6	14.8	38	185
		isopropylbenzene	0.05	160-190	180	24.0	16.1	40.9	185
		n-nonane	0.05	160-190	180	17.9	14.9	38.6	185
9	$(CH_3)_3SiOOC(CH_3)_2C_6H_5$	styrene	0.2	170-210	190	8.6	14.7	39.6	185
		anethole	0.2	170-210	190	18.0	13.3	36.1	7
		n-nonane	0.2	170-210	190	6.6	15.6	41.9	6.7
		heptene-1	0.2	170-210	180	6.7	14.8	40.3	6.7
		triisobutylene	0.2	170-210	190	9.5	11.4	32.7	7

1	2	3	4	5	6	7	8	9	10
		α-methylstyrene	0.2	170–210	190	8.3	14.5	39.4	6.7
		cyclohexene	0.2	170–210	190	13.3	12.6	35.0	6.7
		1.1-diphenylethylene	0.2	170–210	190	15.3	12.1	34.0	6.7
10	$(CH_3)_3SiOOC_4H_9$-n	n-nonane	0.05	180–210	180	4.82	13.9	38.1	155
11	$(CH_3)_3SiOOC_4H_9$-sec	n-nonane	0.05	180–210	180	3.44	13.1	36.7	155
12	$(CH_3)_3SiOOCH(CH_3)C_6H_5$	isopropylbenzene	0.05	180–210	180	4.35	13.8	37.6	186
		n-nonane	0.05	180–210	180	6.17	13.2	36.2	155.186
		anisole	0.05	180–210	180	7.85	12.3	34.1	186
13	$(CH_3)_3SiOOCH(C_6H_5)_2$	n-nonane	0.05	170–210	180	8.44	12.6	34.8	155
14	$(C_2H_5)_3SiOOC(CH_3)_3$	n-decane	0.054	170–210	180	4.79	12.5	32.4	14
		n-decane	0.5	170–200	180	7.67	14.01	34.9	14
		n-decane	0.945	160–200	180	8.94	14.19	36.4	14
		chlorobenzene	0.05	190–220	190	20.0		31.8	190
15	$(C_2H_5)_3SiOOCH(CH_3)C_6H_5$	n-nonane	0.05	170–200	180	16.2	12.1	33.0	186
		anisole	0.05	160–190	180	24.6	13.1	34.6	186
16	$(n\text{-}C_3H_7)_3SiOOCH(CH_3)C_6H_5$	n-nonane	0.05	170–200	180	20.8	12.9	34.4	186
		anisole	0.05	160–190	180	29.7	12.5	33.3	186
17	$C_2H_5(CH_3)_2SiOOC(CH_3)_3$	anisole	0.05		180	4.1	13.0	35.8	144
18	$C_3H_7(CH_3)_2SiOOC(CH_3)_3$	anisole	0.05		180	5.6	15.0	40.0	144
19	$C_4H_9(CH_3)_2SiOOC(CH_3)_3$	anisole	0.05		180	10.0	13.3	35.8	144
20	$C_6H_5CH_2(CH_3)_2SiOOC(CH_3)_3$	anisole	0.05		180	30.8	12.4	33.1	144
21	$C_6H_5(CH_3)_2SiOOC(CH_3)_3$	anisole	0.05		180	21.2	10.5	29.4	144

1	2	3	4	5	6	7	8	9	10
22	$(C_6H_5)_3SiOOC(CH_3)_3$	anisole	0.05	160-190	160	4.1	12.0	32.6	184
23	$(C_6H_5)_3SiOOC(CH_3)_2C_6H_5$	anisole	0.05	150-190	160	6.6	10.5	29.0	184
24	$(C_6H_5)_3SiOOC(C_6H_5)_2CH_3$	anisole	0.05	140-170	160	22.0	10.9	29.0	184
25	$(C_6H_5)_3SiOOC(C_6H_5)_3$	anisole	0.05	100-130	130	26.0	8.9	23.0	184
26	$(CH_3)_2Si\left[OOC(CH_3)_3\right]_2$	anisole	0.05	170-200	180	23.4	13.5	35.6	142
		dimethylphtalate	0.04		190	10.10	14.15	38.4	158
		tetradecane	0.04		190	4.90	13.97	38.7	158
		chlorobenzene	0.04		190	20.00	14.87	39.3	158
		isopropylbenzene	0.2	120-140	140	0.386	12.32	33.5	101
27	$CH_3Si\left[OOC(CH_3)_3\right]_3$	anisole	0.05	160-190	180	93.2	12.6	31.8	142
28	$Si\left[OOC(CH_3)_3\right]_4$	anisole	0.05	110-140	110	21.8	9.6	23.4	142
		isopropylbenzene	0.05	110-140	110	15.1	10.2	24.6	142
29	$CH_2=CHSi(CH_3)_2OOC(CH_3)_3$	isopropylbenzene	0.2	120-140	140	0.03	15.18	41.0	101
30	$CH_2=CHSi(CH_3)(C_2H_5)OOC(CH_3)_3$	isopropylbenzene	0.2	120-140	140	0.221	14.91	38.9	101
31	$CH_2=CHSi(CH_3)(C_2H_5)OOC(CH_3)_2C_2H_5$	isopropylbenzene	0.2	120-140	140	0.411	14.76	38.1	101
32	$CH_2=CHSi(CH_3)(C_2H_5)OOC(CH_3)_2C_6H_5$	isopropylbenzene	0.2	120-140	140	0.714	14.70	37.3	101
33	$CH_2=CHSi(CH_3)(C_3H_7)OOC(CH_3)_3$	isopropylbenzene	0.2	120-140	140	0.017	14.98	41.1	101
34	$CH_2=CHCH_2Si(CH_3)_2OOC(CH_3)_3$	isopropylbenzene	0.2	120-140	140	1.62	11.04	29.9	101

1	2	3	4	5	6	7	8	9	10
35	$CH_2{=}CHSi(CH_3)[OOC(CH_3)_3]_2$	isopropylbenzene	0.2	120-140	140	0.022	11.46	31.1	100.101
36	$CH_2{=}CHSi(CH_3)[OOC(CH_3)_2C_2H_5]_2$	isopropylbenzene	0.2	120-140	140	1.57	10.43	28.8	100.101
37	$CH_2{=}CHSi(C_2H_5)[OOC(CH_3)_3]_2$	isopropylbenzene	0.2	120-140	140	2.59	9.77	26.9	100.101
38	$CH_2{=}CHSi(C_3H_7)[OOC(CH_3)_3]_2$	isopropylbenzene	0.2	120-140	140	0.897	11.71	31.7	100.101
39	$CH_2{=}CHSi(C_3H_7)[OOC(CH_3)_2C_2H_5]_2$	isopropylbenzene	0.2	120-140	140	1.375	10.74	29.5	100.101
40	$CH_2{=}CHSi(CH_3)[OOC(CH_3)_3]_2$	isopropylbenzene	0.2	120-140	140	5.22	8.84	24.8	101
41	$CH_2{=}CHCH_2Si[OOC(CH_3)_3]_3$	isopropylbenzene	0.2	120-140	140	9.58	10.0	26.5	100.101
		chlorobenzene	0.02		189	6.7			190
42	$[(CH_3)_3COOSi(CH_3)_2]_2O$	isopropylbenzene	0.05	200-230	200	8.1	13.1	37.2	164
43	$[C_6H_5(CH_3)_2COOSi(CH_3)]_2O$	isopropylbenzene	0.05	190-220	200	16.0	14.9	40.5	164
44	$[(CH_3)_3COOSi(C_6H_5)_2]_2O$	isopropylbenzene	0.05	180-210	200	38.0	11.7	32.7	164
45	$[C_6H_5(CH_3)_2COOSi(C_6H_5)_2]_2O$	isopropylbenzene	0.05	170-200	200	76.2	13.2	35.2	164
		anisole	0.05	170-200	200	102.3	13.1	34.7	164
46	$(CH_3)_3COOSi[(CH_3)_2O]_6OC(CH_3)_3$	isopropylbenzene	0.05	200-230	200	6.91	13.23	37.7	164
47	 $\left[-Si(CH_3)(OOC(CH_3)_3)-O-\right]_4$	anisole	0.01	190-220	210	28.0	9.1	28	154
		n-nonane	0.01	210-240	210	9.35	12.4	36.3	154
		dodecane	0.01	210-240	210	9.73	11.7	34.7	154

1	2	3	4	5	6	7	8	9	10
48	 $[-Si(CH_3)(OOC(CH_3)_3)-O-]_5$	dodecane	0.01	210–240	210	11.6	10.4	31.7	154
49	 $[-Si(CH_3)(OOC(CH_3)_3)-O-]_6$	dodecane	0.01	210–240	210	11.22	10.8	32.6	154
50	$(CH_3)_3COOSi(CH_3)_2OCH_3$	dimethylphtalate	0.04		190	9.82	14.44	38.4	158
		tetradecane	0.04		190	9.60	14.79	39.8	158
		chlorobenzene	0.04		190	15.20	14.71	39.2	158
51	$C_4H_9O(CH_3)_2SiOOC(CH_3)_3$	anisole	0.05		180	9.8	8.1	25.1	144
52	$ClCH_2(CH_3)_2SiOOC(CH_3)_3$	anisole	0.05		180	15.6	8.4	25.3	144
53	$C_4H_3S(CH_3)_2SiOOC(CH_3)_3$	anisole	0.05		180	62.6	11.1	29.6	144
54	$(CH_3)_3SiOOSi(CH_3)_3$	dimethylphtalate	0.04		190	4.51	15.55	42.1	158
		chlorobenzene	0.05	150–180	150	23		32.1	190
		anisole	0.05	140–170	140	7.2	12.9	32.2	176
		gas phase	0.01	150–180	180	86.0	12.49	32.3	163
55	$(C_2H_5)_3SiOOSi(C_2H_5)_3$	anisole	0.05	110–140	140	136.8	12.3	28.6	176
		gas phase	0.01	120–150	120	11.3	10.4	25.4	163
56	$(n-C_3H_7)_3SiOOSi(n-C_3H_7)_3$	anisole	0.05	110–140	140	143.5	12.4	28.9	176

1	2	3	4	5	6	7	8	9	10
57	$(n\text{-}C_6H_{11})_3SiOOSi(n\text{-}C_6H_{11})_3$	anisole	0.05	110-140	140	127.3	12.4	28.9	176
58	$(C_6H_5)_3SiOOSi(C_6H_5)_3$	anisole	0.05	70-100	100	66.4	12.54	26.8	172.173
59	$\left[C_6H_5(CH_3)_2SiO\ _2\right]$	anisole	0.05	90-120	100	12.4	11.76	26.7	173
		isopropylbenzene	0.05	90-120	100	9.60	12.16	27.6	173
		n-heptane	0.05	90-120	100	6.70	12.39	28.3	173
60	$\left[CH_3(C_6H_5)_2SiO\right]_2$	anisole	0.05	80-110	100	38.1	12.20	26.7	173
61	$\left[C_6H_5CH_2(CH_3)_2SiO\right]_2$	n-heptane	0.05		100	11.75			174
		anisole	0.05		100	20.2	12.6	27.9	174
		tetrahydrofuran	0.05		100	18.0			174
		cyclohexanol	0.05		100	27.0			174
		n-butanol	0.05		100	29.7			174
		cyclohexanone	0.05		100	18.2			174
		isopropanol	0.05		100	22.2	10.8	24.7	174
62	$\left[p\text{-}CH_3C_6H_4(CH_3)_2SiO\right]_2$	anisole	0.05	90-120	100	22.2	11.97	26.7	173
63	$\left[p\text{-}CH_3OC_6H_4(CH_3)_2SiO\right]_2$	anisole	0.05	80-110	110	159.5	12.15	26.62	170
64	$\left[p\text{-}BrC_6H_4(CH_3)_2SiO\right]_2$	anisole	0.05	90-120	110	29.40	12.22	27.69	170
65	$(CH_3)_3SiOOSi(C_6H_5)_3$	1-propanol	0.05		100	25.8	9.4	22.2	174
		acetonitrile	0.05		100	24.6	8.3	20.3	174
		n-heptane	0.05		100	9.2	12.5	28.0	174
			0.05		110	26.6	12.4	28.0	181
		isopropylbenzene	0.05		100	12.0	12.0	27.3	174
			0.05		110	31.6	12.2	27.6	181
			0.05	90-120	100	9.2	12.51	28.2	172

1	2	3	4	5	6	7	8	9	10
		dioxane	0.05		100	14.6	10.2	24.0	174
		anisole	0.05		100	13.4	12.0	27.0	172.174
					110	35.7	12.0	27.1	181
		n-butanol	0.05		100	38.3	-	-	174
		1-propanol	0.05		100	45.2	8.4	20.1	174
		acetonitrile	0.05		100	20.4			174
66	$(C_6H_5)_3SiOOSi(CH_3)_2C_6H_5$	anisole	0.05	80-110	100	32.5	12.07	26.6	172
		isopropylbenzene	0.05	80-110	100	28.7	12.41	27.3	172
		n-heptane	0.05	80-110	100	18.0	12.26	27.3	172
67	$(C_6H_5)_3SiOOSi(CH_3)_2C_6H_4OCH_3$-p	anisole	0.05	70-100	100	119	11.92	25.33	175
68	$(C_6H_5)_3SiOOSi(CH_3)_2C_6H_4CH_3$-p	anisole	0.05	80-110	100	47.0	12.76	27.46	175
69	$(C_6H_5)_3SiOOSi(CH_3)_2C_6H_4Br$-p	anisole	0.05	80-110	100	28.3	11.99	26.54	175
70	$(CH_3)_3SiOOGe(C_6H_5)_3$	n-heptane	0.05	140-170	110	0.12	13.6	34.2	180
		isopropylbenzene	0.05	140-170	110	0.2	13.3	33.2	180
		anisole	0.05	140-170	110	0.24	13.1	32.8	180
			0.05		110	0.25	13.0	32.8	182
71	$(C_2H_5)_3SiOOSi(C_6H_5)_3$	anisole	0.05	120-130	140	36	12.0	29.2	182
72	$(n\text{-}C_3H_7)_3SiOOGe(C_6H_5)_3$	anisole	0.05	120-150	140	34	11.5	28.2	182
73	$(n\text{-}C_4H_9)_3SiOOGe(C_6H_5)_3$	anisole	0.05	110-140	140	58	11.6	28.1	182
74	$(n\text{-}C_5H_{11})_3SiOOGe(C_6H_5)_3$	anisole	0.05	110-140	140	65	12.3	29.3	182

1	2	3	4	5	6	7	8	9	10
75	$(C_6H_5)_3SiOOGe(C_6H_5)_3$	anisole	0.05	90-120	110	28	12.2	27.7	180.182
		isopropylbenzene	0.05	90-120	110	24	12.6	28.4	180
		trichlorobenzene	0.01	180-200	180	0.4			138
					190	1.0			138
					200	6			138
76	$C_6H_5(CH_3)_2SiOOGe(C_6H_5)_3$	n-heptane	0.05	110-140	110	5.72	11.1	27.0	180
		isopropylbenzene	0.05	110-140	110	8.2	11.2	26.8	180
		anisole	0.05	100-130	110	10	11.2	26.6	180
77	$(CH_3)_3SiCH_2CH_2C(0)OOC(CH_3)_3$	isopropylbenzene	0.05	90-110	100	15.0		31.0	38
		n-nonane	0.05	90-110	100	12.7		31.9	38
		chlorobenzene	0.05	80-110	100	19.4		29.0	38
78	$(CH_3)_3SiCH_2CH_2C(0)OOC(CH_3)_2C_6H_5$	isopropylbenzene	0.05	70-100	100	55.3		30.0	38
		nitrobenzene	0.05	70-100	100	51.3		24.0	38
		methanol	0.05	40-70	70	63.9		20.9	38
		tetraethylstannane	0.05	60-90	70	8.6		26.0	38
		tetraethylstannane + phenyl-β-naphtyl-amine			70	2.7			38
79	$(C_2H_5)_3SiCH_2CH_2(0)OOC(CH_3)_3$	isopropylbenzene	0.05	80-110	100	23.4		29.2	38
		nitrobenzene	0.05		100	32.1			38
		acetonitrile	0.05		100	37.3			38
		methanol	0.05	70-100	100	81.5		27.6	38
		methanol + styrene	0.05	80-110	100	39.1		30.3	38
		tetraethylstannane	0.05	70-100	100	107.9		29.9	38
		tetraethylstannane + phenyl-β-naphtyl-amine	0.05		100	25.5			38

1	2	3	4	5	6	7	8	9	10
80	$(C_2H_5)_3SiCH_2C(O)OOC(CH_3)_3$	isopropylbenzene	0.05	100-130	100	2.4		33.8	38
		nitrobenzene	0.05		120	22.9			38
		n-nonane	0.05	100-130	100	2.5			38
		methanol	0.05	90-120	100	8.2			38
		methanol + styrene	0.05	100-130	100	2.2		35.4	38
		tetraethylstannane	0.05	80-100	100	56.5		35.5	38
		tetraethylstannane + phenyl-β-naphtyl-amine	0.05		100	9.5			38
81	$(C_2H_5)_3SiCH_2C(O)OOC(CH_3)_2C_6H_5$	isopropylbenzene	0.05	100-130	100	3.2		27.9	38
		n-nonane	0.05	100-130	100	5.6		33.2	38
		methanol	0.05	60-90	70	11.3		19.6	38
82	$(CH_3)_3SiOCH_2C(O)OOC(CH_3)_3$	isopropylbenzene	0.03		130	35			191
83	$(C_2H_5)_3SiOCH_2C(O)OOC(CH_3)_3$	isopropylbenzene	0.03		130	34.8			191
84	$(CH_3)_2Si[OCH_2C(O)OOC(CH_3)_3]_2$	isopropylbenzene	0.03		130	38.2			191
85	$CH_3(CH_2{=}CH)Si[OCH_2C(O)OOC(CH_3)_3]_2$	isopropylbenzene	0.03		130	39			191
86	$C_6H_5Si[OCH_2C(O)OOC(CH_3)_3]_3$	isopropylbenzene	0.03		130	39			191
87	$Si[OCH_2C(O)OOC(CH_3)_3]_4$	isopropylbenzene	0.03		130	43.5			191

1	2	3	4	5	6	7	8	9	10
88	$(CH_3)_3SiOSi(CH_3)_2OOC(CH_3)_3$	dodecane		200-240	210	15.7	15.6	43.0	193
89	$[(CH_3)_3SiO]_2Si(CH_3)OOC(CH_3)_3$	dodecane		200-240	210	3.6	14.6	42.0	193
90	$[(CH_3)_3SiO]_3SiOOC(CH_3)_3$	dodecane		200-240	210	2.9	14.3	41.7	193
91	$(CH_3)_2(C_6H_5O)SiOOC(CH_3)_3$	chlorobenzene	0.05	190-220	190	22		30.5	190
92	$(CH_3)_3SiOOC_6H_{10}OOC_6H_{10}OOSi(CH_3)_3$	isopropylbenzene	0.05	80-100	80	18.5	11.8	25.1	196
		anisole	0.05	80-100	80	12.1	15.6	31.5	196

$$R_3SiO^\bullet + SH \longrightarrow R_3SiOH + S^\bullet \qquad 3.13$$

$$R'_3CO^\bullet + SH \longrightarrow R'_3COH + S^\bullet \qquad 3.14$$

$$R_3CO^\bullet \longrightarrow R'_2CO + R'^\bullet \qquad 3.15$$

$$R'^\bullet + SH \longrightarrow R'H + S^\bullet \qquad 3.16$$

$$2S^\bullet \longrightarrow S{-}S \qquad 3.17$$

Decomposition products of $Me_3SiOOCMe_2Ph$ are given as an example in Table 3.

TABLE 3
Thermal decomposition products of peroxide
$(CH_3)_3SiOOC(CH_3)_2C_6H_5$ at 200°C (C_0=0.2 mol) (185)

Compound	Yield (in moles per mole of peroxide)		
	anisole	isopropylbenzene	n-nonane
$(CH_3)_3SiOH$	0.82	0.83	0.81
$(CH_3)_6Si_2O$	0.04	0.04	0.07
CH_4	0.65	0.55	0.44
$CH_3COC_6H_5$	0.64	0.54	0.47
$C_6H_5(CH_3)_2COH$	0.22	0.32	0.37
$C_6H_5(CH_3)_2CC(CH_3)_2C_6H_5$	–	0.9	–

Induced free radical decomposition of the peroxide can occur and is a combination of the following reactions (17, 14):

$$R_3SiOOCR'_3 + X^\bullet \longrightarrow HX + R_2(R'_{-H})SiOOCR'_3 \qquad 3.18$$

$$R_3SiOOCR'_3 + X^\bullet \longrightarrow R_3SiOX + R'_3CO^\bullet \qquad 3.19$$

$$R_3SiOOCR'_3 + X^\bullet \longrightarrow R'_3COX + R_3SiO^\bullet \qquad 3.20$$

$$R_2(R'_{-H})SiOOCR'_3 \longrightarrow R_2SiO + R'_3CO^\bullet + R_{-H} \qquad 3.21$$

From $Me_3SiOOCR'_3$ to $Me_2(R)SiOOCR'_3$, where R is another alkyl or aryl group there is a significant competition of reaction 3.9 with reaction 3.10. Composition data of the main products of $R,Me_2SiOOBu$-t conversion are presented in Table 4.

TABLE 4

Products of peroxide thermal conversion ($R_iMe_2SiOOBu$-t, C_o=0.2 mol) in anisole at 180°C (144)

R_i	Yield (in moles per mole of peroxide conversed)				
	acetone	tert-butyl-alcohol	hydroxysilane	$PR^{a)}$	$\frac{K_{3.9}}{K_{3.10}}$
Et	0.470	0.302	0.606	0.220	3.07
Pr	0.258	0.335	indeterm.	0.360	1.50
Bu	0.375	0.429	indeterm	0.148	4.05
$PhCH_2$	0.06	0.073	0.16	0.855	0.16
Ph	0.167	0.161	indeterm.	0.670	0.49
C_4H_3S	0.042	0.055	indeterm.	0.270	0.11

a) PR - the product of R_iOMe_2SiOBu-t rearrangement.

It is obvious from Table 4 that in the competition of reactions 3.9 and 3.10 the rearrangement predominates in the following R_i= $<Bu<Et<Pr<PhCH_2<C_4H_3S$.

Decomposition of peroxides $(C_6H_5)_3SiOOC(CH_3)_n(C_6H_5)_{3-n}$ follows two parallel directions: spontaneous decomposition and rearragement (183, 184). Spontaneous decomposition predominates with increasing n.

Organosilicon peroxides of type R SiOOSiR' undergo rearrangements only:

$$\begin{tikzcd} & R_2(RO)SiOSiR'_3 & 3.22 \\ R_3SiOOSiR'_3 \arrow[ur] \arrow[dr] & & \\ & R_3SiOSi(OR')R'_2 & 3.23 \end{tikzcd}$$

Thermal decomposition of peroxides of type $Ph_3SiOOSbph_4$ proceeds in an analogous way (135):

$$Ph_3SiOOSbPh_4 \longrightarrow Ph_3SiOOSbPh_3(OPh) \qquad 3.24$$

Decomposition of $(Ph_3SiOO)_2SbPh_3$ occurs differently (128):

$$(Ph_3SiOO)_2SbPh_3 \longrightarrow (Ph_3SiO)_2SbPh_3 + O_2 \qquad 3.25$$

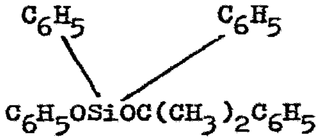
The mechanism of this reaction has not been yet studied.

The rate of rearrangement of R_3EOOER_3 as well as the competition of R-group migration (from the heteroatom to oxygen) are determined by the effective electronegativity of oxygen at the heteroatom (the electronegativity increase is favoured by $d_\pi - p_\pi$ conjugation of the heteroatom with oxygen), nucleophylic reactivity of the R-groups and vacancies in the heteroatom coordination sphere. The difference in the nucleophilicity of the substituents at the heteroatom is responsible for the competition of the possible rearrangement reactions.

The characteristic feature of reaction 3.10, as opposed to reaction 3.9, appears to be the seemingly "rigid" structure of the activated complex (negative entropy of activation), as well as the lower potential barrier of the reaction, i.e., the lower activation energy (Table 5).

TABLE 5

Main products (in moles per mole of the peroxide), kinetic and activation parameters for two stages of $(C_6H_5)_3SiOOC(CH_3)_2C_6H_5$ decomposition in anisole (C_o=0.1 mol/l) (184)

Temperature	$(C_6H_5)_3SiOH$	 C_6H_5 C_6H_5 $C_6H_5OSiOC(CH_3)_2C_6H_5$	$K_{3.10}10^5$ sec^{-1}	$K_{3.9}10^5$ sec^{-1}
160	0.226	0.76	5.1	1.5
170	0.330	0.665	9.7	4.9
180	0.290	0.620	19.1	12.2
190	0.490	0.500	29.6	28.4
		E(kcal/mol)	24	39.2
		ℓgk_o	7.8	15.0

Reactions of type 3.11 occur when CR_3' is CH(Me)Et and, especially, when CR_3' is CH(Me)Ph or $CH(Ph)_2$. Thus, the decomposition products of Me_3SiOOR (Table 6), where R is n-Bu, s-Bu, CH(Me)Ph or $CH(Ph)_2$, indicate that the peroxide decomposition proceeds via competing reactions:

$$Me_3SiOOCHR'R'' \rightarrow Me_3SiO^\bullet + R'R''C(H)O^\bullet \qquad 3.26$$

$$Me_3SiOOCHR'R'' \rightarrow Me_2(MeO)SiOCHR'R'' \qquad 3.27$$

$$Me_3SiOOCHR'R'' \rightarrow Me_3SiOH + R'R''CO \qquad 3.28$$

TABLE 6

Yield of the peroxide thermal decomposition products in n-nonane (C_0= 0.2 mol/l) (in moles per mole of peroxide) (155)

Peroxide	R_3EOH	$(R_3E)_2O$	R'R"CHOH	R"CHO	$RO(R_2)EO$ CHR'R"	R'R"C=O
$(CH_3)_3Si$ OOC_4H_9-n	0.6	0.14	0.34	0.1	-	-
$(CH_3)_3Si$ OOC_4H_9-s	0.21	0.2	0.485	-	0.05	0.13
$(CH_3)_3SiOO$ $CH(CH_3)C_6H_5$	0.75	0.03	0.25	0.07	0.18	0.40
$(CH_3)_3SiOOCH$ $(C_6H_5)_2$	0.52	0.04	0.31	-	0.33	0.38

Thermal decomposition of organosilicon peroxides with more complicated substituents on the Si atom (Table 2) proceeds by combinations of such reactions. However, some characteristic properties are noted for a number of peroxide groups.

Thermal decomposition of organosilicon polyperoxides $R_{4-n}Si$-(OOR')n is characterized by the stepwise cleavage of the first, second, etc. peroxide bonds. This is due to the significant difference of their thermal stability (Table 7).

The rate of thermal decomposition of the first peroxide group increases with increasing n. The effect of the number of peroxy groups on the strength of the peroxy bond is associated with the stability of the radicals which result from the peroxide bond homolysis. From kinetic measurements it follows that the stability of silixy radicals increases with the number of peroxide groups on Si atom.

TABLE 7

Kinetic parameters[*] for decomposition of the first peroxide group of organosilicon polyperoxides in anisole (C_0 = 0.05 mol/l)

N°	Peroxide	$\lg k_0$	E $\frac{Kcal}{mol}$
1	$(CH_3)_3SiOOC(CH_3)_3$	13.9±0.2	37.9±0.5
2	$(CH_3)_2Si[OOC(CH_3)_3]_2$	13.6±0.6	35.6±1.2
3	$(CH_3)Si[OOC(CH_3)_3]_3$	12.7±1.21	31.8±2.4

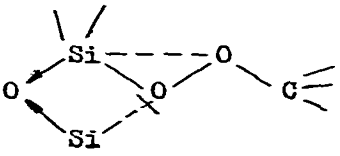
4 $Si[OOC(CH_3)_3]_4$	9.7±0.3 10.2±0.1**	23.4±0.6 24.6±0.2

---

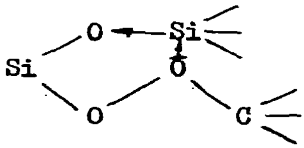
[*] The total expression for the rate constant $k=k_0 \exp\{-E/RT\}$ is derived at 180-210°C for 1, at 170-200°C for 2, at 150-180°C for 3 and 110-140°C for 4.

[**] Kinetic parameters of peroxide 4 in isopropylbenzene.

Organosilicon peroxides of type $[ROOSi(Ri)_2]_2O$ (Table 2, comp. 42-49) have the highest thermal stability. This may be due to enhanced intramolecular coordination between the oxygen atoms of the peroxide group and silicon, facilitated by siloxane bond.



and



Investigations of organosilicon peroxide thermal decomposition have been conducted in viscous and very viscous media. Based on a study of $Me_2Si(OO\ t\text{-}Bu)_2$, it was found that macro- and micro- viscosity has little effect on the peroxide decomposition rate (145). Thus, the changing of the macroviscosity of the medium in the range of 0.18-270 cp essentially does not effect the rate constant of the cleavage of the first peroxide bond on $Me_2Si(OOBu\text{-}t)_2$ (Table 8).

TABLE 8

The effect of medium macroviscosity on the decomposition rate constant (K_1) for $Me_2Si(OOBu\text{-}t)_2$ in n-nonane-polyethylene mixtures at 170°C and C_0 = 0.2 mol/l

Molecular weight of polyethylene	Polyethylene content, weight p.c.	η, cp	10^5K_1, sec^{-1}
3300	0	0.18	4.2
	70	1.0	8.7
	80	3.5	9.0
	85	8.0	9.7
	90	13.0	8.7
	100	18.0	
6500	80	34.0	7.1
	100	2700	5.4

Similarly, kinetic and activation parameters of the first and second peroxide group cleavage for $Me_2Si(OOBu\text{-}t)_2$ are approximately equal for reactions proceeding in solvents significantly different in viscosities (Table 9 and 10).

TABLE 9

Kinetic and activated parameters of $Me_2Si(OOBu\text{-}t)_2$ decomposition in polyethylene and polystyrene

Solvent	C_o $\frac{mol}{l}$	Parameters	Parameter values at temperature, °C 170	180	190	200	210	E_1 $\frac{kcal}{mol}$	ℓgk_{01}	E_2 $\frac{kcal}{mol}$	ℓgk_{02}
Polyethylene	0.05	,cp	270	180	115	55	15				
		$k_1 \cdot 10^5$	5.4	14.9	30.4	80.4	-	37.2	14.1	33.8	12.1
		$k_2 \cdot 10^5$	-	7.2	15.2	34.9	70.2	±1.8	±0.9	±0.8	±0.4
Polystyrene	0.1	$\cdot 10^{-6}$	12.6	4.6	2.2	1.1	0.6				
		$k_1 \cdot 10^5$	5.5	12.9	24.7	55.5	-	32.8	11.8	28.8	9.6
		$k_2 \cdot 10^5$	-	6.8	9.6	24.3	43.8	±1.9	±0.9	±1.5	±0.7

TABLE 10

Kinetic and activated parameters of $Me_2Si(OOBu\text{-}t)_2$ decomposition in alkanes, C_o 0.05 $M^{a)}$

Solvent	Temperature	η, cp	$k_1 \cdot 10^5$ sec^{-1}	E_1 $\frac{kcal}{mol}$	ℓgk_{01}	$k_2 \cdot 10^5$ sec^{-1}	E_2 $\frac{kcal}{mol}$	ℓgk_{02}
Nonane	170	0.180	4.2					
	180	0.165	11.4	34.7±	12.7±	2.7	36.2±	12.8±
	190	0.155	23.7	1.5	0.7	5.0	2.4	1.2
	200	0.145	51.0			13.4		
	210	0.13	-			29.5		
Hexadecane	170	0.446	7.7			-		
	180	0.409	13.4	32.3±	11.7±	2.4	39.9±	14.6±
	190	0.377	30.1	2.4	1.2	5.8	0.9	0.4
	200	0.349	75.6			15.4		
	210	0.323	-			34.4		
Eicosane	170	0.653	5.8			-		
	180	0.598	12.7	33.2±	12.1±	4.6	36.2	13.1±
	190	0.548	30.3	0.9	0.4	11.1	2.4	1.2
	200	0.505	60.1			30.1		
	210	0.467	-			60.5		

Tetra-cosane	170	0.897	10.6	29.5± 1.6	10.6± 0.8	-	-	-
	180	0.817	22.0					
	190	0.747	40.1					
	200	0.684	89.9					

Note: a) E_1 and E_2, logarithms of preexponentials in Table 10 were calculated by the least squares method with indication of mean-root error.

Microviscosity, as it turns out (145) also has a weak influence on the rate of organosilicon peroxide decomposition (Table 11).

TABLE 11
Microviscosity effect on rate constants of $Me_2Si(OOBu\text{-}t)_2$ decomposition in alkanes at 190°C and C_0 0.05 M

Solvent	Viscosity η, cp	$k_1 \cdot 10^2$ sec^{-1}	$k_2 \cdot 10^3$ sec^{-1}
Octane	0.130	31.6	4.1
Nonane	0.155	23.7	5.0
Decane	0.195	21.2	5.4
Dodecane	0.236	24.8	6.7
Hexadecane	0.377	30.1	5.8
Eicosane	0.548	30.36	11.1
Tetracosane	0.747	40.1	-
Tetracosane-nonane	0.403	39.9	

The behavior of organosilicon peroxides in olefins is different than in saturated hydrocarbons. As mentioned above (see "Physical Properties"), the organic peroxides of the silicon subgroup elements form donor-acceptor complexes with olefins. In case of silicon peroxide these complexes do not show up in the thermochemical measurements but manifest themselves in kinetic studies (Table 12).

TABLE 12
Kinetic parameters of $(CH_3)_3SiOOC(CH_3)_3$(1) and $(CH_3)_3SiOOC(CH_3)_2$-C_6H_5(2) peroxide decomposition in olefins, C_0 =0.2 mol/l. Temperature of decomposition is 170 - 210°C (6)

Olefin	1			2		
	ℓgk_o	E, kcal/mol	$\Delta S^{\neq}$, e.u	ℓgk_o	E, kcal/mol	$\Delta S^{\neq}$, e.u
n-Nonane*	14.5	41.1	+5.1	15.6	41.9	+10.0
Heptane-1	14.0	38.8	+2.6	14.8	40.3	+6.5
α-Methylstyrene	13.1	36.6	-1.4	14.5	39.4	+5.0
Styrene	-	-	-	-	-	-
Cyclohexene	10.0	31.7	-11.1	12.6	35.0	-3.5
1.1-Diphenyl-ethylene	9.9	29.1	-16.2	12.1	34.0	-6.1

* The data are given for comparison.

The composition of organosilicon peroxide decomposition products in olefins (Table 13) is indicative of a free radical mechanism for the total process.

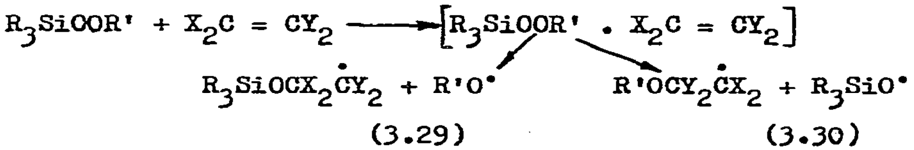
TABLE 13

The main decomposition products of $Me_3SiOOCMe_2Ph$ in olefins (in moles per mole of peroxide) (C_o=0.2 mol.l^{-1}, T = 200°C) (7)

Solvent	Me_3SiOH	$Ph\overset{\overset{O}{\|}}{C}Me$	$PhMe_2COH$	$MeO-\underset{Me}{\overset{Me}{Si}}OCMe_2Ph$	Addition product	
					$Me_3SiO^{\bullet}$	$PhMe_2CO^{\bullet}$
n-Nonane[a)]	0.67	0.48	0.19	0.3	absent	absent
α-Methyl-styrene	0.08	0.48	0.11	0.27	0.65	0.14
Styrene	0.11	0.47	0.05	0.27	0.83	not determined
Tri-isobutylene	0.35	0.5	0.2	0.3	0.35	absent
Cyclohexene	0.65	0.26	0.54	0.22	0.12	
1.1-Diphenyl-ethylene	0.02	0.65	absent	0.07	0.9	0.28

a) These data are listed for comparison.

The process can be pictured in terms of the following main reactions:



(3.29) (3.30)

$$R_3SiO^\bullet + SH \longrightarrow R_3SiOH + S^\bullet \qquad 3.31$$

$$R_3SiO^\bullet + X_2C = CY_2 \longrightarrow R_3SiOCX_2\dot{C}Y_2 \qquad 3.32$$

$$R'O^\bullet + SH \longrightarrow R'OH + S^\bullet \qquad 3.33$$

$$R'O^\bullet + X_2C = CY_2 \longrightarrow R'OCX_2\dot{C}Y_2 \qquad 3.34$$

In the competition reaction of $k_{3.32}/k_{3.31}$ and $k_{3.34}/k_{3.33}$ was determined for a series of olefins (Table 14) (72).

TABLE 14

The dependence of $k_{3.32}/k_{3.31}$ and $k_{3.34}/k_{3.33}$ upon $R_3EO^\bullet$ and solvent at 25°C, C_0=0. 1 mol/l

Radical	$k_{3.32}/k_{3.31}$; $k_{3.34}/k_{3.33}$					
	Nonane	1-nonane	1-heptene	1-hexene	Cyclohexene	2.3-dimethyl-1.3-butadiene
Ph_3SiO	0	0.69	1.74	-	1.00	-
Et_3SiO	0	0.69	1.72	1.74	1.00	24.0
Me_3SiO	0	-	1.83	-	-	
Et_3GeO	0	-	0.43	-	0.43	22.0
Me_3GeO	0	-	0.37	-	-	-
Me_3CO	0	0	0	0	0	0.2
$PhMe_2CO$	0	0	0	0	0	1.0

Table 14 shows that for $Et_3SiO^\bullet$ the ratio $k_{3.32}/k_{3.31}$ decreases in the series 1-hexene > 1-heptene > 1-nonane. As the number of methylene groups in the olefin increases, the probability of reaction 3.31 increases.

The temperature has a substantial effect on the $k_{3.32}/k_{3.31}$ ratio (Table 15).

TABLE 15
Activation parameters of competing reactions of hydrogen addition and abstraction by $Me_3SiO^\bullet$ radical in a solution of 1-heptene (72), $Me_3SiOOSiMe_3$ (1), $Me_3SiOOCMe_2Ph$ (2)

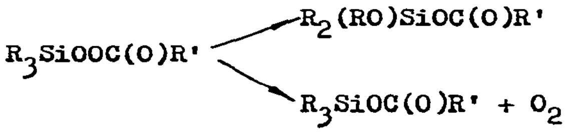
Activation Parameters	Peroxide (1) mol/l		Peroxide (2) mol/l	
	0.1	0.2	0.1	0.2
$E_{3.31} - E_{3.32}\ \frac{kcal}{mol}$	1.5	1.4	1.4	1.3
$k_{3.32}/k_{3.31}$ a)	14.7	15.6	15.9	14.9

a) $k_{3.32}$ and $k_{3.31}$ are preexponentials of the hydrogen addition and abstraction reactions, respectively.

The nature of this reaction is such that with increasing temperature the ratio $k_{3.32}/k_{3.31}$ decreases.

ORGANOSILICON ACYLPEROXIDES $R_3SiOOC(O)R'$

Silicon acylperoxides are unstable at room temperature (46, 48, 129). Their decomposition proceeds by parallel paths:

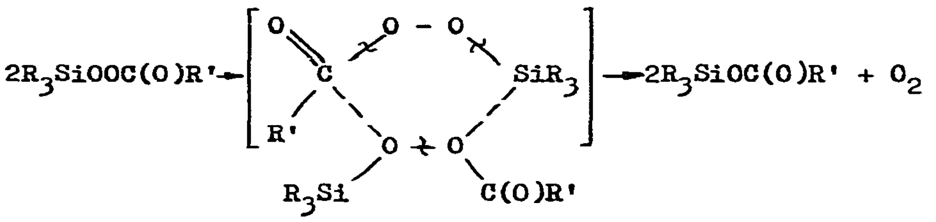


$$R_3SiOOC(O)R' \longrightarrow R_2(RO)SiOC(O)R' \qquad 3.35$$

$$R_3SiOOC(O)R' \longrightarrow R_3SiOC(O)R' + O_2 \qquad 3.36$$

When R is aryl, only the acyl peroxide rearrangement takes place; when R is alkyl, the acyl peroxide decomposition proceeds simultaneously by both pathways.

The mechanism of the silicon acyl peroxide rearrangement is identical to that of the organosilicon peroxide rearrangement. The silicon acyl peroxide decomposition proceeds via a cyclic activated complex with oxygen evolution:



3.37

SILICON-SUBSTITUTED CARBONIC PERACID ESTERS OF THE TYPE $R_3Si-(CH_2)_n\ C(O)OOR'$

Such peroxides are thermally rather stable. Their decomposition proceeds at a measurable rate at temperatures above 100°C (38, 124, 160). The nature of the decomposition products (Table 16) is indicative of free radical mechanism. Spontaneous perester decomposition via peroxide bond cleavage results in generation of radicals:

$$R_3Si(CH_2)_nCH_2C(O)OOC(Me)_2R' \rightarrow R_3Si(CH_2)_nCH_2C(O)O^\bullet + R'Me_2CO^\bullet \qquad 3.38$$

where R = Me, Et; R' = Me, Et, Ph; n = 0, 1, 2.

The reactions below then follow:

$$R_3Si(CH_2)_nCH_2C(O)O^\bullet \rightarrow R_3Si(CH_2)_n\dot{C}H_2 + CO_2 \qquad 3.39$$

$$R'Me_2CO^\bullet \xrightarrow{SH} R'Me_2COH + S^\bullet \qquad 3.40$$

$$R'Me_2CO^\bullet \rightarrow R'COMe + Me^\bullet \qquad 3.41$$

$$R_3Si(CH_2)_n\dot{C}H \xrightarrow{SH} R_3Si(CH_2)_nCH_3 + S^\bullet \qquad 3.42$$

Only a part of the trialkylsilylalkyl radicals dimerizes or disproportionates:

$$2R_3Si(CH_2)_n\dot{C}H_2 \rightarrow [R_3Si(CH_2)_nCH_2]_2 \qquad 3.43$$

$$2R_3Si(CH_2)_n\dot{C}H_2 \xrightarrow[n=1]{} R_3SiCH_2CH_3 + R_3SiCH{=}CH_2 \qquad 3.44$$

The mechanism of $R_3Si(CH_2)_nCH_2C(O)OOCMe_2R'$ decomposition in tetraethyltin solution seems to be essentially analogous. A distinguishing characteristic of the process in this case is a considerable contribution from induced perester decomposition by triethylstannyl radicals:

$$(CH_3)_3SiCH_2CH_2C(O)OOC(CH_3)_3 + (C_2H_5)_3Sn^\bullet \longrightarrow$$
$$\longrightarrow (CH_3)_3SiCH_2CH_2C(O)OSn(C_2H_5)_3 + {}^\bullet OC(CH_3)_3 \qquad 3.45$$

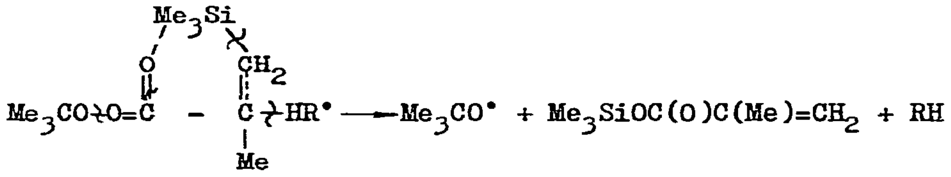
TABLE 16

Thermal decomposition products of $RC(O)OOC(CH_3)_3$

Reaction Products	R is $(C_2H_5)_3SiCH_2$			R is $(C_2H_5)_3SiCH_2CH_2$			R is $(CH_3)_3SiCH_2CH_2$			
	n-nonane	cumene	$(C_2H_5)_4Sn$	cumene	chloro-benzene	$(C_2H_5)_4Sn$	n-nonane	cumene	chloro-benzene	$(C_2H_5)_4Sn$
	T = 130°C			T = 110°C			T = 120°C			
	Yield, moles/mol of initial perester									
CO_2	0.65	0.88	0.31	0.75	0.74	0.35	0.85	0.60	0.72	0.36
$(CH_3)_3COH$	0.55	0.55	0.65	0.82	0.42	0.95	0.44	0.60	0.44	0.93
$(CH_3)_2CO$	0.10	0.36	-	0.20	0.36	-	0.20	0.40	0.61	-
CH_4	0.39	0.31	-	0.20	0.31	-	0.10	0.42	0.65	-
C_2H_6	-	-	0.16	-	-	0.08	0.20	-	-	0.18
C_2H_4	-	-	0.55	-	-	0.62	-	-	-	0.62
$RC(O)OH$	0.27	0.14	-	0.24	0.23	-	0.10	0.33	0.23	0.29
RH	0.50	0.70	0.30	0.59	0.18	0.33	0.36	0.45	0.10	0.29
R - H	-	-	-	trace	0.18	-	-	-	-	-
R - R	0.04	0.04	-	0.05	0.05	-	0.09	-	-	-
$ROC(CH_3)_3$	-	-	-	-	0.10	-	-	-	-	-
$R - C_6H_4Cl$	-	-	-	-	-	-	-	-	0.20	-
$R_2 - C_6H_3Cl$	-	-	-	-	0.10	-	-	-	-	-
$R - OSn(C_2H_5)_3$	-	-	0.65	-	-	0.64	-	-	-	0.42
$(C_2H_5)_3SnOC(CH_3)_3$	-	-	0.30	-	-	-	-	-	-	-

$Me_3SiCH_2CH_2C(O)OOCMe_3$ decomposition in hexaethylditin proceeds radically. An unusual perester rearrangement with R_3Si group migration from carbon to oxygen has been discovered on investigation of the decomposition of the α-methyl β-(trimethylsilyl)propionic peracid t-butyl ester in a number of organic solvents (123).

$$Me_3SiCH_2CH(Me)C(O)OOCMe_3 + R^\bullet \longrightarrow$$



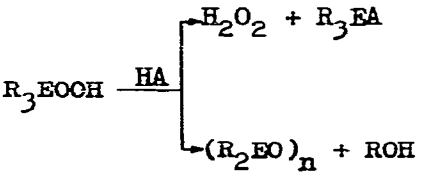
$$Me_3CO\!-\!O{=}\overset{\overset{Me_3Si}{O}}{C} - \underset{Me}{\overset{CH_2}{C}}\!-\!HR^\bullet \longrightarrow Me_3CO^\bullet + Me_3SiOC(O)C(Me){=}CH_2 + RH \qquad 3.46$$

Cumyl esters of γ-(trimethylsilyl)- and γ-(dimethylphenylsilyl) propionic peracids in methanol undergo heterolytic rearrangement with phenyl group migration from carbon to oxygen (124).

$$R_3Si(CH_2)_2CH_2C(O)OOCMe_2Ph \longrightarrow R_3Si(CH_2)_2CH_2C(O)OC(OPh)Me_2 \qquad 3.47$$

CATALYTIC DECOMPOSITION

The catalytic decomposition of organosilicon peroxides has received little study. In the presence of strong acids (HA), hydroperoxides decompose with loss of active oxygen (177, 179).



$$R_3EOOH \xrightarrow{HA} H_2O_2 + R_3EA \qquad 3.48$$

$$R_3EOOH \xrightarrow{HA} (R_2EO)_n + ROH \qquad 3.49$$

If E is Ge or Sn, the first reaction prevails, but if E is Si, both reactions proceed simultaneously. However, acids do not effect the rate of decomposition of triphenylsilyl hydroperoxide in 1.2-dichlorobenzene (55).

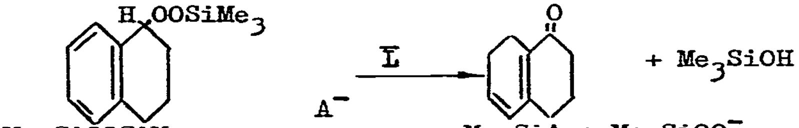
Some nucleophiles (anions of organic and mineral acids and others catalyze the isomerization of organosilicon hydroperoxides or peroxides to non-peroxidic products (54, 55, 86, 134, 177).

$$R_3SiOOH \xrightarrow{y^-} R_2(RO)SiOH \qquad 3.50$$

$$ArMe_2SiOOSiMe_2Ar \xrightarrow{y^-} Me_2(ArO)SiOSiArMe_2 \qquad 3.51$$

$$Ph_3SiOOGePh_3 \xrightarrow{y^-} Ph_2(PhO)GeOSiPh_3 \qquad 3.52$$

The rate determining step of reactions 3.50 - 3.52 seems to be coordination of nucleophilic ligand (y^-) at the heteroatom as it occurs in the case:Group 4 organic peroxides with other Lewis bases (olefins, amines, pyridines) (6, 7). Yet in the presence of Lewis bases the nature of the organosilicon peroxide decomposition depends on the type of peroxide. Other types of decomposition are also known (30, 48, 60).



3.53

$$Me_3SiOOSiMe_3 \xrightarrow{A^-} Me_3SiA + Me_3SiOO^- \qquad 3.54$$

Complex silicon-organomercury peroxides decompose readily with formation of free mercury in the presence of many nucleophilic additives (amines, pyridines, alcohols and so on) 5, 11).

$$R_3SiHgOOSiR_3 \xrightarrow{L} R_3SiOOSiR_3 + Hg \qquad 3.55$$

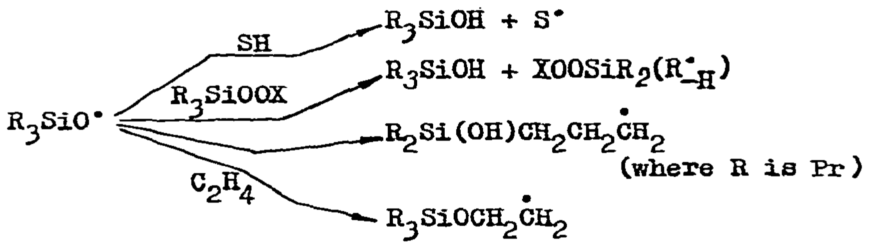
PHOTODECOMPOSITION

Organosilicon peroxides are unstable to UV-irradiation (50, 55). Their photodecomposition proceeds with homolysis of the peroxide bond:

$$R_3SiOOR' \xrightarrow{h\nu} R_3SiO^\bullet + R'O^\bullet \qquad 3.56$$

where R is Me, Et, Pr; R' is t-Bu or SiR_3.

On photolysis of such peroxides in an organic medium the resulting $R_3SiO^\bullet$ and $R'O^\bullet$ radicals take part in the usual radical reactions, the competitions of their reactions depending upon the nature of the initial peroxide, the solvent and other factors. For example, for trialkylsilixy radicals (R_3SiOOX photolysis in cyclopentane or in cyclopropane, temperature -120° to -20°C), the following reactions can compete:



3.57
3.58
3.59
3.60

REACTIONS WITH ORGANIC AND INORGANIC COMPOUNDS

Such reactions of organosilicon peroxides can occur with retention or with loss of the peroxide function. However, quantitative physicochemical data on these reactions are not available. In the most cases the mechanism has not been investigated.

Organosilyl peroxides react reversibly with mineral and organic acids:

$$R_3SiOOH + HX \rightleftharpoons R_3SiX + H_2O_2 \qquad 3.61$$

$$R_3SiOOR' + HX \rightleftharpoons R_3SiX + R'OOH \qquad 3.62$$

$$R_3SiOOSiR_3 + HX \rightleftharpoons R_3SiX + H_2O_2 \qquad 3.63$$

where X is OH, OC(O)R' , halogen, etc.

Although quantitative data on these equilibria are lacking, it has been noted (1, 13, 41, 48), that organosilicon peroxide hydrolysis is negligible under normal conditions.

Organosilicon peroxides with an Si–Cl linkage, e.g., $Me_3COOSiRR'Cl$, silylate compounds containing active hydrogen atoms and other functional groups which can react with chlorosilanes (98).

Trimethylsilyl peroxide reacts with sodium ethoxide to give Si – O bond heterolysis (23, 24):

$$Me_3SiOOSiMe_3 + NaOEt \longrightarrow Me_3SiOONa + Me_3SiOEt \qquad 3.64$$

Si – O bond heterolysis also occurs on treatment of R_3SiOOR' and $Si(OOR')_4$ with alcohols (19, 48, 112). The reaction proceeds quantitatively in acetic acid and in the presence of catalytic amounts of sulfuric acid.

$$R_3SiOOR' + R''OH \xrightarrow{H^+} R''OOR' + R_3SiOH \qquad 3.65$$

$$Si(OOR')_4 + R''OH \xrightarrow{H^+} Si(OH)_4 + R''OOR' \qquad 3.66$$

Sb - O bond heterolysis occurs in reactions of $Ph_3SiOOSbPh_4$ with water or with acids (135):

$$Ph_3EOOSbPh_4 + HX \longrightarrow Ph_3EOOH + Ph_4SbX \qquad 3.67$$

(X is Cl, HO.)

Triethylsilyl peroxide reacts with lead tetra-acetate, chromic oxide and triphenyl-carbinol in ice acetic acid (29). The stoichiometry of these reactions is very complicated and their mechanisms have not been investigated.

On the basis of the reaction products isolated, the above-mentioned reactions are believed to proceed with Si - O bond cleavage.

In contrast to its carbon analog, trimethylsilyl peroxide reacts readily with alkali metals, tetracarbonylnickel, sulfur dioxide and sulfur trioxide at room temperature or below 0°C (29, 30):

$$Me_3SiOOSiMe_3 + 2M \longrightarrow 2Me_3SiOM \qquad 3.68$$

$$Me_3SiOOSiMe_3 + Ni(CO)_4 \longrightarrow (Me_2SiO)_2Ni + 4CO \qquad 3.69$$

$$Me_3SiOOSiMe_3 + SO_2 \longrightarrow Me_3SiOS(O)_2OSiMe_3 \qquad 3.70$$

$$Me_3SiOOSiMe_3 + 2SO_3 \longrightarrow Me_3SiOS(O_2)OOS(O_2)OSiMe_3 \qquad 3.71$$

These reactions proceed with peroxide bond cleavage. However, the mechanisms of these peroxide conversions have been investigated.

The reaction of $Me_3SiOOCMe_3$ with $NaHSO_3$ (19, 47) and those of bis(trimethylsilyl)peroxymonosulfate with hydrogen halides, alkali metal halides and pyridine also proceed with peroxide bond cleavage (35).

Triphenylsilyl hydroperoxide and a hemiacetal were found to react with retention of the peroxide function (131):

$$Ph_3SiOOH + Cl_3CCH(OH)OCH_3 \longrightarrow Ph_3SiOOCH(CCl_3)OH + H_3COH \qquad 3.72$$

REACTIONS WITH ORGANOELEMENT COMPOUNDS

The investigations of reactions of organosilicon peroxides with organoelement compounds are few in number and non-systematic.

Oxidative addition of triphenylsilyl peroxide to triphenylphosphine and triphenylstibine is known (128):

$$Ph_3SiOOH + Ph_3E \longrightarrow Ph_3E(OH)OSiPh_3 \qquad 3.73$$

where E is P or Sb.

Trimethylsilyl peroxide reacts readily with nucleophilic organoelement reagents with peroxide bond cleavage (29, 30):

$$Me_3SiOOSiMe_3 + BuLi \longrightarrow Me_3SiOBu + Me_3SiOLi \qquad 3.74$$

$$Me_3SiOOSiMe_3 + RMgX \longrightarrow Me_3SiOR + Me_3SiOMgX \qquad 3.75$$

$$Me_3SiOOSiMe_3 + NaAlH_2(OCH_2CH_2OMe)_2 \longrightarrow$$
$$\longrightarrow H_2 + NaAl(OSiMe_3)_2(OCH_2CH_2OMe)_2 \qquad 3.76$$

$$Me_3SiOOSiMe_3 + Ph_3E \longrightarrow Me_3SiOSiMe_3 + Ph_3EO \qquad 3.77$$

where E = P, As, Sb

$$Me_3SiOOSiMe_3 + R_2S \longrightarrow Me_3SiOSiMe_3 + R_2SO \qquad 3.78$$

Reactions of tert-butylperoxytrimethylsilane with Ph_3P, Ph_3As and $(EtO)_3P$ proceed similarly (34). The mechanisms of these reactions have not been investigated.

Organosilicon hydroperoxides retain their peroxide function in some reactions, 3.79 - 3.82 :

$$Ph_3SiOOH + R_3SiCl \longrightarrow Ph_3SiOOSiR_3 + HCl \qquad 3.79$$

(R = alkyl, aryl, aralkyl) (140, 152, 165, 167, 168, 169, 171, 172, 180).

$$Ph_3SiOOH + Ph_4SbX \longrightarrow Ph_3SiOOSbPh_4 + HX \qquad 3.80$$

(X = Cl or Br) (128).

$$Ph_3SiOOH + Et_3Tl \longrightarrow Ph_3SiOOTlEt_2 + C_2H_6 \quad (130) \qquad 3.81$$

$$2Ph_3SiOOH + Ph_3SbO \longrightarrow (Ph_3SiOO)_2SbPh_3 + H_2O \quad (128) \qquad 3.82$$

APPLICATIONS OF ORGANOSILICON PEROXIDES

The first communication on organosilicon peroxides (22) pointed to their applications as polymerization catalysts and oxidizing agents. Almost all patents on peroxide synthesis contain information on tests for practical utilization.

The most important application of organosilicon peroxides is their use as initiators of polymerization processes (44, 45, 59, 74, 83-85, 109, 118). The problem of decreasing residual monomer content is one of the most important in polymer production. Unsaturated compounds remaining in the polymer cause deterioration of the physico-mechanical characteristics of final product (shock resistance, transparency, rupture resistance and so on). Organosilicon peroxides have allowed us to make progress in solving this problem (76-80). Styrene and its derivatives can be polymerized in the presence of tert-butylperoxytrimethylsilane, alone or along with a standard peroxide, to give polymers (molecular weight 40,000--80,000) which contain 0.03 - 0.6 per cent residual monomer (78). The use of standard organic peroxide initiators leads to polymers with no less than 0.5 per cent residual monomer. Polymerization of styrene containing tert-butylperoxytrimethylsilane (0.001, 0.005, 0.01 and 0.02 parts by weight, respectively) in alternative temperature conditions (80) produces polymers with monomer contents of 0.69, 0.42, 0.09 and 0.05 per cent, respectively.

Bis(tert-butylperoxy)dimethylsilane (0.08 parts) is dissolved in 100 parts of styrene to give a polymer which contains 0.02 per cent of monomer (79). Other polymers were similarly prepared using the same quantity of p-chlorostyrene, o-, m-, and p-methylstyrene, mixtures of styrene and acrylonitrile or of styrene and α-methylstyrene. Other catalysts mentioned were tris(tert-butylperoxy)methylsilane, tetrakis (tert-butylperoxy)silane, bis(tert-butylperoxy)-methylphenylsilane and tris(tert-butylperoxy)phenylsilane (79).

Glossy polymers free from haze and colour with self-lubricating properties have been prepared by the bulk polymerization of styrene and (or) acrylonitrile in the presence of bis(tert-butylperoxy)dimethylsilane and polyethylene glycol or polypropylene glycol (77). Organosilicon peroxides act effectively at a high degree of polymerization, at high temperature, and result in an increased degree of monomer conversion.

Production of high pressure polyethylene is an important commercial process in which organosilicon peroxide initiators also can be used. tert-$BuOOSiMe_3$, $(tert\text{-}BuOO)_2SiMe_2$ and $(tert\text{-}BuOO)_2SiPh_2$ have been used to polymerize ethylene at 146-85°/20000 psi. These organoperoxysilanes possess the usual advantages of peroxide polymerization initiators, but they decompose more slowly at high temperatures and thus are more effective than the usual organic initiators for preparing highly branched polyethylene having a narrow molecular weight distribution (108).

Oligomeric organosilicon peroxides of general formula $R_3COO-(-SiR_2O-)_nSiR_2OOCR_3$ have been used as initiators to increase the process rate and to improve the composition of the final product in olefin polymerization by the high pressure method (156, 157).

Peroxides are the only vulcanizing agents for saturated polymers which are free of double bonds that can be attacked by sulfur (75, 105). In this application organosilicon peroxides are promising. Compounds of formula $Y(OSiR_2)_nOOR'$ were proposed for hardening silicon compounds to obtain elastic materials (25, 26). As vulcanizing agents, organosilicon peroxides $CH_2{=}CHCH_2SiR_m(-OOCR_3-)_n$, $CH_2{=}CHSiR_m(OOCR_3)_n(n+m=3)$ (189), $R'_a\ R''_b\ Si(OOCR_3)_{4-a-b}$ (88), $R_nX_{3-n}SiR'OOR''$ (117) and silyl-acylperoxy compounds (45) were also used.

Organosilicon peroxides were used in cross-linking polyolefins (68, 104). This avoided the offensive odor which is characteristic of polymer samples cross-linked in the presence of dicumyl peroxide and mechanical properties were conserved. A blend of peroxides having different decomposition temperature ranges was also used for cross-linking polyethylene (27). This blend gave a cross-linking rate intermediate between those of either peroxide alone. The combination affords a cross-linking system for almost any conceivable time-temperature requirement.

One promising method for the modification of synthetic materials is the introduction of peroxide groups into an oligomeric chain. These generate free macroradicals when heated and on recombination of the latter a three-dimensional structure forms. Organopolysiloxanes have been prepared with a given number of peroxide groups regularly distributed in the chain. These could be vulcanized and co-vulcanized without application of vulcanizing agents (95).

The formation of a peroxidative aerosil has been proposed by treatment of the aerosil with an organosilicon peroxide (94). Such aerosils may be used as a reinforcing and, simultaneously, cross-linking filler for various polymeric systems, in particular silicone rubbers (93, 97).

SKTV-1 vulcanisation has been studied in the presence of various organosilicon peroxides (106, 107). It was found that rubbers formed with the help of organosilicon peroxides are somewhat inferior in rupture resistance to rubbers containing dicumyl peroxide as the controlling vulcanizing agent. However, relative elongation and elasticity of filled rubber is higher than that of vulcanizers obtained with the help of dicumyl peroxide. Heat aging of rubbers at temperatures around 300° during 60 - 120 hours occur more slowly if rubber vulcanization is conducted in the presence of peroxides such as $Me_2Si(OOCMe_3)_2$, $[Si(OOCMe_3)_2O]_{4-6}$ and $[SiMe(OOCMe_3)O]_{4-6}$.

Spectroscopic investigations of vulcanizates showed that the cyclic organosilicon structure of the peroxide which had decomposed had been preserved. Probably, this is responsible for the elasticity and the thermal stability of rubbers formed.

Fan and Shaw studied organosilicon peroxides as cross-linking agents for high pressure polyethylene (107). For $Me_{4-n}Si(OOCMe_2Ph)_n$ -type peroxides the cross-linking efficiency decreased with increasing peroxide group number "n". In the $Me_{4-n}Si(OOCMe_3)_n$ series it increased with increasing n and reached a maximum when n=3.

The vulcanizing capability of $RSi(OOCMe_3)_3$ is little affected with changing R. In the past decade there have been many studies concerning the capability of peroxides to promote adhesion. For example, for combination with metal surfaces, polyolefins are combined with organoelement peroxides of general formula $R_nX_mE(OOR')_p$, where E = Si, Ge, Sn, Pb, As or Sb (136). The layers glued under pressure at temperatures of 160-240° have interlaminar strength of 3-5 kg/cm. The layer strength without peroxide addition is 1.5 kg/cm. Reinforced plastics with high mechanical strength have been prepared by coating glass fibers with tris(α-cumylperoxy)vinylsilane (which functions as an adhesive and a polymerization initiator), contacting with unsaturated polyesters and curing (71). Laminates for low-temperature use, e.g. in vehicle windshields, were made from an adhesive or a nonirradiated vinyl acetate-ethylene copolymer and a silyl peroxide (146, 147). Peroxides of type $R_mR'_{4-n-m}Si(OOR\ )_n$ were used for combining elastomers with various materials on vulcanization (111, 150). Elastomers were combined with ferrous and non-ferrous metals, wood, glass, ceramics, cord, PVC, polyolefins and resins. The combination has high mechanical properties and is stable toward various media. Adhesives based on organosilicon peroxide compounds also are used for agglutinating metals, glass, plastics, cellulose and other solid materials (43, 63).

Fan and Shaw have conducted systematic investigations of the adhesive properties of organosilicon peroxides (62-67, 69). They found relations between peroxide structure and its capability to promote adhesion. For $R_{4-n}Si(OOR')_n$ peroxides the efficiency of promoting adhesion increases with increasing n.

Compounds containing a tert-alkylperoxy group on silicon atom are more effective promoters of adhesion than arylalkylperoxysilanes. All other things being equal, the efficiency of promoting adhesion by $R_{4-n}Si(OOR')_n$ is higher if R is an unsaturated group (vinyl, allyl and so on). The authors proposed a mechanism of adhesion promotion with organosilicon peroxides which involved the formation of Si-O-Si, Si-O-M linkages (M is metal) or Si-O-C on the interface (62).

Organosilicon peroxides form a new class of adhesion promoters which differ from the well-known adhesive agents. They can be used in those cases where cross-linking and promotion of adhesion are required simultaneously. In addition to the above mentioned fields organosilicon peroxides may be used as oxidizing agents (22, 52, 84), fuel additives (84), as well as flame-retardants (102).

The first instances of commercial silylperoxide production have been recorded. Union Carbide Corp. has registered vinyltri (tert-butylperoxy)silane as a commercial product Y-5712; Kayaku Noury Co. advertises the same product under the trade-name Koyabutyl C (153).

REFERENCES

1 W. Adam, J.-C. Liu, J. Amer. Chem. Soc., 94(1972)2894.

2 W. Adam, H.C. Steinmetzev, Angew. Chem., Chem., 84(1972)590, Intern. Ed., 11(1972)540.

3 Yu.A. Alexandrov, J. Organometal. Chem., 55(1973)1.

4 Yu.A. Alexandrov, Zhydkophasnoye avtookisleniye elementoorganicheskikh soyedinenii, M., "Nauka", 1978, 130 pp.

5 Yu.A. Alexandrov, V.N. Glushakova, G.A. Rasuvaev, J. Organometal. Chem., 40(1972)49.

6 Yu.A. Alexandrov, V.V. Gorbatov, V.G. Tsvetkov, N.V. Yablokova, Dokl. Akad. Nauk SSSR, 234(1977)896.

7 Yu.A. Alexandrov, V.V. Gorbatov, N.V. Yablokova, V.G. Tsvetkov, J Organometal. Chem., 157(1978)267.

8 Yu.A. Alexandrov, V.P. Maslennikov, J. Organometal. Chem. Library, 3(1977)75.

9 Yu.A. Alexandrov, V.P. Maslennikov, J. Organometal. Chem. Library, 3(1977)103.

10 Yu.A. Alexandrov, V.P. Maslennikov, N.V. Sergeyeva, J. Organometal. Library, 5(1977)219.

11 Yu.A. Alexandrov, G.A. Razuvaev, V.N. Glushakova, G.N. Figurova, Dokl. Akad. Nauk SSSR, 185(1969)1293.

12 Yu.A. Alexandrov, V.A. Shushunov, Zh. Obshch. Chim., 35(1965)115.

13 Yu.A. Alexandrov, B.V. Suldin, Trudy po khimii i khim. tekhnol. (Gorky), vyp. 2(1964)358.

14 Yu.A. Alexandrov, B.V. Suldin, Trudy po khimii i khim. tekhnol. (Gorky), vyp. 1(1965)69.

15 Yu.A. Alexandrov, B.V. Suldin, V.A. Shushunov, Trudy po khimii i khim. tekhnol., Gorky, vyp. 2(1968)17.

16 Yu.A. Alexandrov, B.V. Suldin, V.A. Shushunov, Zh. Obshch. Khim., 39(1969)2364.

17 Yu.A. Alexandrov, B.V. Suldin, V.A. Shushunov, "Uspekhi khimii organicheskikh perekisnykh soyedinenii i avtookisleniya", M., "Khimiya", 1969, p.224.

18 Yu.A. Alexandrov, V.G. Tsvetkov, V.V. Gorbatov, N.V. Yablokova, Zh. Obshch. Khim., 48(1978)1134.

19 M.M. Azanovskaya, Yu.A. Oldekop, A.N. Kharitonovich, "Sb. nauchnykh rabot instituta physico-organicheskoi khimii AN BSSR, vyp. 8(1960)32.

20 A.E. Batog, O.M. Mashchenko, M.K. Romanzevich, USSR author's certificate N°.179770, Bulletin of Inventions N°.6(1966).

21 I.Yu. Belavin, Yu.I. Baukov, I.F. Lutsenko, USSR author's certificate N°.451703, Bulletin of Inventions N°.44(1974).
22 K.L. Berry, US Patent N°.2692887 (1954), Chem. Abstr., 49, 13290g(1955).
23 A. Blaschette, Z. Anorg. Allgem. Chem. 384(1971)177.
24 A. Blaschette, Angew. Chem. 83(1971)548, Inter. Ed., 10(1971)522.
25 B.A. Bluestein, US Patent N°.2970982(1961), RZh. Khim., 18T138 (1963).
26 B.A. Bluestein, BRD Patent N°.1138946 (1963).
27 A.C. Bluestein, R.F. Grossman, US Patent N°.3661877 (1972), Chem. Abstr., 77, 4949v (1972).
28 N.G. Bokii, V.E. Shklover, Yu.T. Struchkov, Itogi nauki i tekhniki, Krystallokhimiya, 10, 94, izd. VINITI, M., 1974.
29 D. Brandes, A. Blaschette, J. Organometal. Chem., 49(1973) C6.
30 D. Brandes, A. Blaschette, J. Organometal. Chem., 73(1974)217.
31 D. Brandes, A. Blaschette, J. Organometal. Chem., 78(1974)1.
32 D. Brandes, A. Blaschette, Z. Naturforsch. 29b(1974)797, RZh. Khim. 11B, 392 (1975).
33 D. Brandes, A. Blaschette, Monatsch. Chem., 106(1975)1299.
34 D. Brandes, A, Blaschette, J. Organometal. Chem., 99 (1975)C 33.
35 B. Bressel, A. Blaschette, Z. Anorg. Allgem. Chem., 377(1970)182.
36 B. Bressel, A. Blaschette, Z. Anorg. Allgem. Chem., 377(1970)196.
37 T.N. Brevnova, N.F. Cherepennikova, N.S. Vyazankin, Zh. Obshch. Khim., 44(1974)1937.
38 T.N. Brevnova, O.F. Rachkova, N.F. Cherepennikova, N.S. Vyazankin, Zh. Obshch. Khim., 44(1974)1771.
39 T.N. Brevnova, T.F. Rachkova, N.S. Vyazankin, Zh. Obshch. Khim., 39(1969)1788.
40 T.N. Brevnova, O.F. Rachkova, N.S. Vyazankin, Zh. Obshch. Chem., 40(1970)1760.
41 T.G. Brilkina, V.A. Shushunov, Trudy po khimii i khim. tekhnol. (Gorky), vyp. 3(1960)505.
42 T.G. Brilkina, V.A. Shushunov, Reaktsii metalloorganicheskikh soyedinenii s kislorodom i perekisyami, M., "Nauka", 1966.
43 Great Britain Patent N°.1288268 (1972).
44 Great Britain Patent N°.1360755 (1975).
45 Great Britain Patent N°.1366386 (1974).
46 E. Buncel, A.G. Davies, Chem. Ind. (London) (1957)492.
47 E. Buncel, A.G. Davies, Chem. Ind. (London) (1958)1052.
48 E. Buncel, A.G. Davies, J. Chem. Soc. (1958)1550.

49 P.G. Cookson, A.G. Davies, N.A. Fazal, J. Organometal. Chem., 99(1975)C 31.

50 P.G. Cookson, A.G. Davies, N.A. Fazal, B.P. Roberts, J. Amer. Chem. Soc., 98(1976)616.

51 R.C.P. Cubbon, Progr. React. Kinet., 5(1970)29.

52 R.L. Dannley, W.A. Aue, G.C. Farrant, US Patent N°.3458546, Chem. Abstr., 71, 102016 (1969).

53 R.L. Dannley, G.C. Farrant, J. Org. Chem., 34(1969)2432.

54 R.L. Dannley, G. Yalics, J. Org. Chem., 30(1965)2417.

55 R.L. Dannley, G. Yalics, 1. Org. Chem., 30(1965)3848.

56 A.G. Davies in D. Swern "Organic Peroxides", Vol.2, Wiley-Interscience, New York, 1971, p.338.

57 A.G. Davies, E. Buncel, Chem. Ind. (London) (1956)1052.

58 A.G. Davies, E. Buncel, J. Chem. Soc., (1958)1550.

59 A.G. Davies, E. Buncel, Great Britain Patent N°.827366 (1960), Chem. Abstr., 54, 14097f (1960).

60 A.G. Davies, C.H. Hall, J. Chem. Soc., (1959)3835.

61 A.N. Yegorochkin, N.S. Vyasankin, S.Ya. Khorshev, S.Ye. Skobeleva, V.A. Yablokov, A.P. Tarabarina, Dokl. Akad. Nauk SSSR, 194, N°.6, (1970)1326.

62 Y.-L. Fan, Adhesion, 4, N°.3(1972)261.

63 Y.-L. Fan, R. Greggshaw, US Patent N°.3856606 (1974) RZh. Khim., 9N 105P (1976).

64 Y.-L. Fan, R.G. Shaw, Aerosp. Adhes. Elastomers, Nat SAMPE Tech. Conf. Proc., 2nd 1970, 537.

65 Y.-L. Fan, R.G. Shaw, BRD Patent N°.1930574 (1969), Chem. Abstr., 72, 67082h (1970).

66 Y.-L. Fan, R.G. Shaw, Modern Plast., 47, N°.5 (1970)104.

67 Y.-L. Fan, R.G. Shaw, Proc. Anniv. Conf., Soc. Plast. Ind., Reinf. Plast/Compos. Div., 25th 1970, 16-A, 6 pp.

68 Y.-L. Fan, R.G. Shaw, US Patent N°.3631161 (1971), RZh. Khim., 18 S 448 P (1972).

69 Y.-L. Fan, R.G. Shaw, Rubber World, 164(1971)56.

70 Y.-L. Fan, R.G. Shaw, J. Org. Chem., 38(1973)2410.

71 J. Gaehde, J. Dahlmann, DDR Patent 74344 (1970), Chem. Abstr., 74, 64948a (1971).

72 V.V. Gorbatov, N.V. Yablokova, Yu.A. Alexandrov, Zh. Obshch. Khim., 48(1978)2061.

73 P. Groth, Acta Chem. Scand., 21(1967)2608, 2631, 2695, 2711; 23(1969)1311.

74 W. Hahn, Z. Metzinger, Macromol. Chem., 21(1956)113, Chem. Abstr., 51(1957)7296.
75 G.A. Harpell, Rubber World, 1974, 171, N°.1, 69, 71; RZh. Khim., 1 N 141 (1976).
76 A.F. Harris, US Patent N°.3385911 (1968), Chem. Abstr., 69, 20020j (1968).
77 A.F. Harris, US Patent N°.3385912 (1968), Chem. Abstr., 69, 20021k (1968).
78 A.F. Harris, G.A. Mortimer, France Patent 1383459, Chem. Abstr., 63, 13448d (1965).
79. A.F. Harris, G.A. Mortimer, France Patent 1441172, Chem. Abstr., 66, 29410g (1967).
80 A.F. Harris, G.A. Mortimer, US Patent N°.3297669 (1967), RZh. Khim., 14 S 135 P (1968).
81 R.R. Hiatt, Canad. J. Chem., N°.5, 42, (1964)985.
82 R.H. Hunt, R.A. Leacock, C.W. Peters, K.T. Hecht, J. Phys. Chem., 42(1965)1931.
83 H. Jenkner, BRD Patent N°.1019305 (1957), Chem. Abstr., 54, 1304b (1960).
84 H. Jenkner, BRD Patent N°.1030345 (1960), RZh. Khim., 17 L 115 (1961).
85 J.R. Joy, US Patent N°.3772349 (1973).
86 G.S. Kalinina, T.A. Basalgina, N.S. Vyazankin, G.A. Razuvaev, V.A. Yablokov, N.V. Yablokova, J. Organometal. Chem., 96(1975)213.
87 D. Käss, H.Oberham, D. Brandes, A. Blaschette, J. Mol. Struct., 40(1977)65.
88 K. Kawazumi, K. Hashi, S. Horii, Japan Patent 1795 (1966), Chem. Abstr., 65, 13928 (1966).
89 K. Kawazumi, B. Murai, Bull. Chem. Soc. Jap., 39(1966)1951.
90 S.Ya. Khorshev, A.N. Yegorochkin, S.Ye. Skobeleva, N.P. Sluchevskaya, A.V. Ganyushkin, V.A. Yablokov, Zh. Obshch. Khim., 48(1978) 1353.
91 S.Ya. Khorshev, S.Ye. Skobeleva, A.N. Yegorochkin, N.P. Sluchevskaya, N.V. Yablokova, V.A. Yablokov, Zh. Obshch. Khim., 47(1977) 1357.
92 Ye.G. Kiparisova, I.B. Rabinovich, Dokl. Akad. Nauk SSSR, 199, N°.5 (1971)1075.
93 A.K. Litkovets, L.K. Yeryomina, V.D. Lobkov, M.P. Grinblat, A.V. Karlin, N.V. Khaber, F.I. Tzyupko, T.I. Kotovich, M.I. Khomay, Zh. N. Kostyakova, I.G. Grinevich, N.T. Timofeyevich, in "Issled.

v obl. phis. i khimii kauchukov i resin", L., 1975, 281, RZh. Khim., 4T 349(1976).

94 A.K. Litkovets, M.P. Grinblat, V.I. Vatamanyuk, F.I. Tzyupko, M.I. Khoma, N.T. Timofeyevich, L.K. Yeryomina, R.N. Galkin, T.I. Kotovich, author's certificate of the USSR N°.532601, Bulletin of Inventions N°.39 (1976).

95 A.K. Litkovets, A.V. Karlin, V.D. Lobkov, N.I. Klim, Kh.S. Sidorak, author's certificate of the USSR N°.476292, Bulletin of Inventions N°.25 (1975).

96 A.K. Litkovets, N.I. Klim, F.I. Tzyupko, O.I. Gevus, A.N. Karpenko, I.S. Oleksin, author's certificate of the USSR 455601, Bulletin of Inventions, N°.8 (1977).

97 A.K. Litkovets, V.D. Lobkov, A.V. Karlin, Zh.N. Parchevskaya, M.P. Grinblat, F.I. Tzyupko, A.M. Berjoza, I.G. Grinzevich, author's certificate of USSR N°.504817, Bulletin of Inventions, N°.8 (1976).

98 A.K. Litkovets, F.I. Tzyupko, N.I. Klim, I.S. Oleksin, O.I. Gevus, Yu.V. Savitsky, Vestnik Lvovskogo Polytechn. Instituta, N°.96 (1975)129.

99 A.K. Litkovets, T.I. Yurzhenko, Dokl. Akad. Nauk SSSR, 142 (1962)1316.

100 A.K. Litkovets, T.I. Yurzhenko, Dokl. Akad. Nauk SSSR, 154, N°.3 (1964)679.

101 A.K. Litkovets, T.I. Yurzhenko, "Usp. khim. org. perikisnykh soyedin. i avtookisleniya." Dokl. vses. konf., 1965, "Khimiya", Moscow, 1969, 77 pp., Chem. Abstr., 72, 79152 1(1970).

102 O.L. Mageli, R.E. Light, E.J. Varnagy, US Patent N°.3338864 (1967), Chem. Abstr., 67, 91391a (1967).

103 A.P. Marjin, V.A. Yablokov, A.N. Sunin, Yu.A. Shlyapnikov, Izv. Akad. Nauk SSSR, Ser. Khim., (1975)2251.

104 S. Matsumura, H. Miyauchi, M. Yoshida, Y. Nakashio, BRD Patent N°.2064114 (1971), Chem. Abstr., 76, 46885g (1972).

105 V.E. Mikhlin, S.V. Petrova, M., NIITeKhim 1974, 54 p.

106 V.E. Mikhlin, N.P. Sluchevskaya, D.Ya. Zhinkin, T.M. Antonova, A.V. Ganyushkin, Informatsionyi bulleten po khim. prom. SEV. M., 1977, N°.6 (69), p.28.

107 V.E. Mikhlin, V.A. Yablokov, T.M. Antonova, A.V. Tomadze, manuscript dep. in NIITeKhim (Cherkassy), N°.11, p.272.

108 G.A. Mortimer, US Patent N°.3450686 (1969); Chem. Abstr., 71, (1969).

109 M. Nakano, Yu. Minoura, Kogyo Kogaku Zasshi, 70 (11) (1967)1935.

110 M.D. Newton, W.A. Zathan, W.Y. Hehre, J.A. Pople, J. Chem. Phys., 52 (1970)4064.

111 C.H. Nitzsche, BRD Patent N°.2141879 (1973); Chem. Abstr., 79, 6534e (1973).

112 Yu.A. Ol'dekop, M.M. Azanovskaya, A.N. Kharitonovich, Zh. Obshch. Khim., 31 (1961)126.

113 Yu.A. Ol'dekop, F.E. Livshits, Zh. Obshch. Khim., 44 (1979)2174.

114 Yu.A. Ol'dekop, F.Z. Livshits, USSR author's certificate N°.456809, Bulletin of Inventions N°.2 (1975).

115 Yu.A. Ol'dekop, F.Z. Livshits, L.V. Bereznevich, Izv. Akad. Nauk BSSR, Ser. Khim., N°.4 (1975)113, RZh. Khim., 3Zh384 (1976).

116 R.L. Ostrozynski, US Patent 3700712 (1972) RZh. Khim., 17N 108P (1973).

117 W.J. Owen, B.E. Cooper, Great Britain Patent N°.1400713 (1975) RZh. Khim., 7N 149P (1976).

118 W.J. Owen, B.E. Cooper, BRD Patent 2247885 (1973); Chem. Abstr., 79, 19634n (1973).

119 R.A. Pike, L.H. Shaffer, Chem. Ind. (London) (1951)1294.

120 V.A. Puchin, G.A. Petrovskaya, L.P. Mamchur, A.N. Karpenko, Zh. Org. Khim., 12, N°.2 (1976)328.

121 I.B. Rabinovich, E.G. Kiparisova, Yu.A. Alexandrov, Dokl. Akad. Nauk SSSR, 200 (1971)1116.

122 G.A. Razuvaev, Yu.A. Alexandrov, V.N. Glushakova, G.N. Figurova, Dokl. Akad. Nauk SSSR, 185 (1969)1293.

123 G.A. Razuvaev, T.N. Brevnova, N.F. Cherepennikova, N.P. Makarenko, Zh. Obshch. Khim., 47 (1977)97.

124 G.A. Razuvaev, T.N. Brevnova, N.F. Cherepennikova, S.Kh. Ratushnaya, Zh. Obshch. Khim., 46 (1976)857.

125 G.A. Razuvaev, T.N. Brevnova, V.V. Semyonov, Zh. Obshch. Khim., 47 (1977)2270.

126 G.A. Razuvaev, T.G. Brilkina, Izv. Akad. Nauk SSSR, Ser. Khim., 1975, 1769.

127 G.A. Razuvaev, T.G. Brilkina, Usp. Khim., 14 (1976)2196.

128 G.A. Razuvaev, T.G. Brilkina, E.V. Krasil'nikova, T.I. Zinov'eva, A.I. Filimonov, J. Organometal. Chem., 40 (1972)151.

129 G.A. Razuvaev, V.A. Dodonov, N.I. Mysin, T.I. Starostina, Zh. Obshch. Khim., 42 (1972)152.

130 G.A. Razuvaev, V.A. Dodonov, T.I. Starostina, T.A. Ivanova, J. Organometal. Chem., 37 (1972)233.

131 G.A. Razuvaev, V.A. Dodonov, S.N. Zaburdayeva, Ye.A. Pavlenko, Zh. Org. Khim., 8 (1972)1818.
132 G.A. Razuvaev, V.A. Shushunov, V.A. Dodonov, T.G. Brilkina, in D. Swern "Organic Peroxides", Vol.3, Wiley-Interscience, New York, 1972, p.141.
133 G.A. Razuvaev, V.A. Yablokov, A.V. Ganyushkin, V.E. Shklover, I.I. Tsinkler, Yu.T. Struchkov, Dokl. Akad. Nauk SSSR, 242 (1978)132.
134 G.A. Razuvaev, V.A. Yablokov, A.V. Ganyushkin, N.V. Yablokova, G.S. Kalinina, J. Organometal. Chem., 165 (1979)281.
135 G.A. Razuvaev, T.I. Zinov'yeva, T.G. Brilkina, Dokl. Akad. Nauk SSSR, 188 (1969)830.
136 W. Reicherdt, K. Wunsch, DDR Patent 61866 (1968) RZh. Khim., 18S 587P (1969).
137 G.M. Rubottom, M.J. Loper Nieves, Tetrahedron Lett. (1972)2423.
138 A.K. Shubber, R.L. Dannley, J. Org. Chem., 36 (1971)3784.
139 A. Simon, H. Arnold, J. Prakt. Chem., 8 (1959)241.
140 S.Ye. Skobeleva, S.Ya. Khorshev, V.A. Yablokov, A.N. Sunin, Zh. Obshch. Khim., 45 (1975)585.
141 S.Ye. Skobeleva, N.S. Vyazankin, S.Ya. Khorshev, A.N. Yegorochkin, V.A. Yablokov, A.P. Tarabarina, A.N. Sunin, N.V. Yablokova, Zh. Obshch. Khim., 43 (1973)1514.
142 N.P. Sluchevskaya, V.A. Yablokov, N.V. Yablokova, Yu.A. Alexandrov, Zh. Obshch. Khim., 46 (1976)1540.
143 N.P. Sluchevskaya, V.A. Yablokov, N.V. Yablokova, Yu.A. Alexandrov, Zh. Obshch. Khim., 46 (1976)2724.
144 N.P. Sluchevskaya, N.V. Yablokova, V.A. Yablokov, Yu.A. Alexandrov Zh. Obshch. Khim., 48 (1978)1136.
145 N.P. Sluchevskaya, N.V. Yablokova, V.A. Yablokov, Yu.A. Alexandrov, Zh. Obshch. Khim., 48 (1978)2511.
146 R.H. Snedeker, K.T. Garty, F.J. Skiermont, US Patent N°.3622440 (1971), Chem. Abstr., 76, 100779y (1972).
147 R.H. Snedeker, K.T. Garty, F.J. Skiermont, US Patent N°.3666614 (1972), Chem. Abstr., 77, 62955p (1972).
148 N.A. Sokolov, Yu.A. Alexandrov, Usp. Khim., 47 (1978)307.
149 G. Sosnovsky, J.H. Brown, Chem. Rev., 66 (1966)529.
150 K.G.Steinfort, C.H. Nitzschs, BRD Patent N°.2137681 (1973); Chem. Abstr., 79, 6557q (1973).
151 A.P. Tarabarina, V.A. Yablokov, Zh. Obshch. Khim., 40 (1970) 2334.

152 A.P. Tarabarina, V.A. Yablokov, N.V. Yablokova, Zh. Obshch. Khim., 40 (1970)1094.

153 "Technocrat", 1976, 9, N°.5, 79; RZh. Khim. 2N 102P (1977).

154 A.V. Tomadze, V.A. Yablokov, N.V. Yablokova, Yu.A. Alexandrov, Zh. Obshch. Khim., 47 (1977)2549.

155 A.V. Tomadze, V.A. Yablokov, N.V. Yablokova, Yu.A. Alexandrov, sb. "Khimia EOS", vyp. 5 (1977)47.

156 O.N. Tzvetkov, Ye.N. Grigoryeva, N.N. Komarova, V.N. Monastyrsky, A.P. Golosov, Ye.I. Sembay, I.I. Gavlo, author's certificate of USSR N°.486027, Bulletin of Inventions N°.36 (1975).

157 O.N. Tzvetkov, Ye.N. Grigor'yeva, N.N. Komarova, V.N. Monastyrsky, Ye.I. Sembay, I.I. Gavlo, author's certificate of USSR N°.527443, Bulletin of Inventions N°.33 (1976).

158 A.A. Turovsky, V.V. Petrenko, N.A. Turovsky, A.K. Litkovets, Zh. Obshch. Khim., 47 (1977)2556.

159 M.R. Vilenskaya, G.A. Petrovskaya, L.P. Mamchur, Zh. Obshch. Khim., 48 N°.8 (1978)1735.

160 N.S. Vyazankin, G.A. Razuvaev, T.N. Brevnova, Dokl. Akad. Nauk SSSR, 163 (1965)1389.

161 V.A. Yablokov, N.V. Alkeeva, A.P. Tarabarina, A.V. Tomadze, N.V. Yablokova, Yu.A. Alexandrov, Zh. Obshch. Khim., 44 (1974) 1789.

162 V.A. Yablokov, A.V. Ganyushkin, Yu.A. Alexandrov, Zh. Org. Khim., 11 (1975)2285.

163 V.A. Yablokov, A.V. Ganyushkin, N.V. Yablokova, Zh. Obshch. Khim., 47 (1977)2553.

164 V.A. Yablokov, A.V. Ganyushkin, N.V. Yablokova, V.E. Mikhlin, T.M. Antonova, Zh. Obshch. Khim., 47 (1977)1786.

165 V.A. Yablokov, S.A. Khorshev, A.P. Tarabarina, A.N. Sunin, Zh. Obshch. Khim., 43 (1973)607.

166 V.A. Yablokov, N.P. Sluchevskaya, N.V. Yablokova, Ye.N. Chernyshev, V.I. Savushkina, Zh. Obshch. Khim., 47 (1977)229.

167 V.A. Yablokov, A.N. Sunin, Zh. Obshch. Khim., 42 (1972)472.

168 V.A. Yablokov, A.N. Sunin, Zh. Obshch. Khim., 42 (1972)2499.

169 V.A. Yablokov, A.N. Sunin, Zh. Obshch. Khim., 43 (1973)1061.

170 V.A. Yablokov, A.N. Sunin, A.V. Ganyushkin, Zh. Obshch. Khim., 44 (1974)287.

171 V.A. Yablokov, A.N. Sunin, G.A. Fedostseva, Zh. Obshch. Khim., 44 (1974)1945.

172 V.A. Yablokov, A.N. Sunin, L.Ya. Isayeva, N.I. Kostina, Zh. Obshch. Khim., 43 (1973)1305.

173 V.A. Yablokov, A.N. Sunin, G.N. Saikina, A.V. Ganyushkin, Zh. Obshch. Khim., 43 (1973)1308.
174 V.A. Yablokov, A.N. Sunin, N.V. Yablokova, Yu.A. Alexandrov, Zh. Obshch. Khim., 46 (1976)2726.
175 V.A. Yablokov, A.N. Sunin, N.V. Yablokova, A.V. Ganyushkin, Zh. Obshch. Khim., 44 (1974)2163.
176 V.A. Yablokov, A.N. Sunin, N.V. Yablokova, A.V. Ganyushkin, Zh. Obshch. Khim., 44 (1974)2446.
177 V.A. Yablokov, A.P. Tarabarina, "Kinetics and Catalysis", 10 (1969)200.
178 V.A. Yablokov, A.P. Tarabarina, D.A. Kreknin, Zh. Obshch. Khim., 40 (1970)2255.
179 V.A. Yablokov, A.P. Tarabarina, N.V. Yablokova, "Trudy po khimii i khim. technol., Gorky, vyp. 2(1970)167.
180 V.A. Yablokov, A.P. Tarabarina, N.V. Yablokova, Zh. Obshch. Khim., 42 (1972)157.
181 V.A. Yablokov, A.P. Tarabarina, N.V. Yablokova, M.I. Stalnova, Zh. Obshch. Khim., 41 (1971)887.
182 V.A. Yablokov, A.P. Tarabarina, N.V. Yablokova, A.V. Tomadze, Zh. Obshch. Khim., 43 (1973)1311.
183 V.A. Yablokov, A.P. Tarabarina, N.V. Yablokova, A.G. Zezina, Zh. Obshch. Khim., 42 (1972)2480.
184 V.A. Yablokov, A.P. Tarabarina, N.V. Yablokova, Zh. Obshch. Khim., 42 (1972)1051.
185 V.A. Yablokov, N.V. Yablokova, A.P. Tarabarina, M.N. Shemuranowa, Zh. Obshch. Khim., 41 (1971)1565.
186 V.A. Yablokov, N.V. Yablokova, A.V. Tomadze, Yu.A. Alexandrov, Zh. Obshch. Khim., 45 (1975)588.
187 T.I. Yurzhenko, G.I. Yelagin, Yu.V. Savitsky, A.K. Litkovets, A.N. Karpenko, author's certificate of USSR N°.414226, Bulletin of Inventions, N°.5 (1974).
188 T.I. Yurzhenko, A.K. Litkovets, Dokl. Akad. Nauk SSSR, 136 (1961) 1361.
189 T.I. Yurzhenko, A.S. Novikov, A.K. Litkovets, L.M. Chebysheva, author's certificate of USSR N°.156673, Bulletin of Inventions, N°.5 (1963).
190 V.V. Petrenko, A.A. Turovsky, A.K. Litkovets, Ukr. Khim. Zh., N°.9, 45 (1979)894.
191 V.A. Fomin, V.S. Etlis, I.I. Khelimskaya, T.I. Radbil, sb. "Khimia EOS". vyp. 7 (1979)56.

192 L.M. Terman, T.N. Brevnova, O.D. Sutina, V.V. Semenov, A.V. Ganyushkin, Izv. Akad. Nauk SSR, Ser. Khim., (1980)629.

193 V.A. Yablckov, A.V. Tomadze, N.V. Yablokova, Yu.A. Alexandrov, Zh. Obshch. Khim., 49 (1979)1787.

194 A.K. Litkovets, F.I. Tsyupko, Ya.T.Timofeyevich, Vestnik Lvovskogo Politekhn. Instituta, N°.137 (1979)156.

195 R. Halle, L.A. Bock, W. Greek, US Patent 4161485 (1979), RZh. Khim., 3N 129P (1980).

196 N.P. Sluchevskaya, N.V. Yablokova, L.A. Granik, V.A. Yablokov, Yu.A. Alexandrov, Zh. Obshch. Khim., 49 (1979)1255.

197 A.V. Tomadze, N.V. Yablokova, V.A. Yablokov, Zh. Obshch. Khim., 49 (1979)1171.