[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

The Mechanism of the Acid- and Base-catalyzed Equilibration of Siloxanes

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The base-catalyzed equilibration of hexamethyldisiloxane (MM) and octamethylcyclotetrasiloxane (D_4) has been observed to proceed at a reasonable rate at 80° with solid tetramethylammonium hydroxide as catalyst. A maximum viscosity has been observed after several hours but, on further reaction, the viscosity eventually decreased to the value which was found by Scott in the case of sulfuric acid equilibration. The presence of the viscosity maximum is interpreted by assuming that $(CH_3)_2SiO$ units react more rapidly than $(CH_3)_3SiO_{1/2}$ units under the conditions of the experiment. A reinvestigation of the acid-catalyzed equilibration of hexamethyldisiloxane and octamethylcyclotetrasiloxane has shown that no viscosity maximum occurs in this case. The equilibration of siloxanes using tetramethylammonium hydroxide as catalyst has also been extended to include the systems D_4 and octamethyltrisiloxane (MDM), D_4 and decamethyltetrasiloxane (MD_2M), and hexamethylcyclotrisiloxane (D_3) and MM. The reactivity of siloxanes toward bases has been determined to decrease in the order $D_3 > D_4 > MD_2M > MDM > MM$.

Introduction

In his classic work on the equilibration of M- and D-units,[1] Scott[2] studied systems consisting of equimolar mixtures of hexamethyldisiloxane (MM) and octamethylcyclotetrasiloxane (D_4) employing a sulfuric acid catalyst.[3-5] However, in the past, base-catalysis of systems consisting of M and D containing compounds has received little attention.[6,7] In the present study, the authors have investigated the base-catalyzed equilibration of a one-to-one molar solution of hexamethyldisiloxane (MM) and octamethylcyclotetrasiloxane (D_4) with 0.1% tetramethylammonium hydroxide catalyst at 80°. Also in the present series of experiments, the studies have been extended to include the following systems: octamethyltrisiloxane (MDM) and D_4 with 0.1% tetramethylammonium hydroxide at 80°, decamethyltetrasiloxane (MD_2M) and D_4 with 0.1% of tetramethylammonium hydroxide at 80°, MM and hexamethylcyclotrisiloxane (D_3) with 4% sulfuric acid at room temperature and several other acid-catalyzed systems. The effects of the reactant structures and molar ratios, the effect of the catalyst, and the conditions of equilibration upon the reaction have been investigated.

Experimental

Preparation of Siloxanes.—D_4 was obtained by the hydrolysis of dimethyldichlorosilane[8-10] followed by careful drying and fractionation. The crude D_4 obtained in this fashion was dried over calcium hydride and redistilled, b.p. 175° at 755 mm. and n^{20}_D 1.3968 (previous lit. values b.p. 175°,[11] n^{20}_D 1.3968[12]). MDM and MD_2M were obtained by the method of Patnode and Wilcock[13] and each of these crude compounds was then dried over calcium hydride and distilled. The physical properties of these compounds were: MDM, b.p. 91° at 106 mm., n^{20}_D 1.3850 (previous lit. values b.p. 99° at 154 mm.[14] and n^{20}_D 1.3848[13]); MD_2M, b.p. 113° at 57 mm. and 193° at 758 mm., n^{20}_D 1.3895 (previous lit. values b.p. 194° at 760 mm.,[13] n^{20}_D 1.3895[13]). D_3 was obtained from the pyrolysis of polydimethylsiloxane fluids[13] and this compound was purified as previously described,[15] m.p. 64–65° (previous lit. value 65°[15]). Decamethylcyclopentasiloxane (D_5) was prepared in a manner analogous to that employed for the preparation of D_4. The physical properties of D_5 were: b.p. 90° at 10 mm., n^{20}_D 1.3981 (previous lit. values b.p. 210° at 760 mm.,[13] n^{20}_D 1.3982[13]).

Calcium hydride was found to be an effective drying agent for siloxanes and after distillation the siloxanes were free of traces of alkali. Thus, samples of D_4 purified by this method had excellent physical properties[12] and moreover, the vapor pressure of a sample was constant while being maintained at 140° for 24 hours.

Preparation of Catalyst.—Eastman Kodak Company "White Label" 10% aqueous tetramethylammonium hydroxide was evaporated *in vacuo* and finally pumped on a high vacuum line at room temperature. The solid which remained analyzed for 66.1% tetramethylammonium hydroxide but contained 8.2% of tetramethylammonium carbonate, 25% water, and 0.5% sodium and 0.008% potassium (the last two values were determined by means of a flame photometer).[16] The percentages of hydroxide and carbonate were determined by titrating a sample with standard hydrochloric acid using phenolphthalein and methyl orange as indicators. Titration of a sample with Karl Fischer reagent gave the combined percentages of water and hydroxide. This material was found to be suitable as a basic siloxane rearrangement catalyst and gave homogeneous solutions in siloxanes at 80°.

Equilibration of MM and D_4 with Base.—In the initial series of experiments, equimolar mixtures of MM and D_4 were treated with 0.1% tetramethylammonium hydroxide. The siloxane solutions were maintained at 80.0 ± 0.1° in sealed containers. At various times, samples were withdrawn, and the viscosities of these samples were determined after treating them as described below. At 80°, tetramethylammonium hydroxide dissolved in the siloxane medium, and the system to be studied was homogeneous.

In order to stop the reaction of the base with the siloxanes at the time at which the sample was withdrawn, a procedure for removal of tetramethylammonium hydroxide was developed. Each sample was withdrawn from the reaction flask and immediately treated with an equal volume of aqueous 3 *N* HCl. The acid was then separated, and the oil was washed with water until the *p*H increased to about 4. Each of the samples was then dried over anhydrous sodium carbonate and finally allowed to stand for several hours over diatomaceous silica (Johns–Manville Celite-270). The oil

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[1] For convenience the abbreviations M and D will be used to represent $(CH_3)_3SiO_{1/2}$ and $(CH_3)_2SiO$ units, respectively. For a complete discussion of the use of this shorthand notation, *cf.* E. G. Rochow, "The Chemistry of the Silicones," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1951, p. 79 *et seq.*

[2] D. W. Scott, THIS JOURNAL, **68**, 2294 (1946).

[3] W. I. Patnode and D. F. Wilcock, *ibid.*, **68**, 362 (1946).

[4] F. P. Price, *ibid.*, **70**, 871 (1948).

[5] D. F. Wilcock, *Gen. Elec. Rev.*, **49**, [No. 11], 14 (1946).

[6] J. F. Hyde, U. S. Patent 2,490,357 (December 6, 1949).

[7] J. F. Hyde, U. S. Patent 2,567,110 (September 4, 1951).

[8] W. I. Patnode and D. F. Wilcock, THIS JOURNAL, **68**, 360 (1946).

[9] M. J. Hunter, J. F. Hyde, E. L. Warrick and H. J. Fletcher, *ibid.*, **68**, 667 (1946).

[10] M. J. Hunter, E. L. Warrick, J. F. Hyde and C. C. Currie, *ibid.*, **68**, 2284 (1946).

[11] C. A. Burkhard, E. G. Rochow, H. S. Booth and J. Hart, *Chem. Revs.*, **41**, 97 (1947).

[12] R. C. Osthoff and W. T. Grubb, THIS JOURNAL, **76**, 399 (1954).

[13] W. I. Patnode and D. F. Wilcock, *ibid.*, **68**, 358 (1946).

[14] D. F. Wilcock, *ibid.*, **68**, 691 (1946).

[15] R. C. Osthoff, W. T. Grubb and C. A. Burkhard, *ibid.*, **75**, 2227 (1953).

[16] This tetramethylammonium hydroxide (27.4% H_2O) was not a pure hydrate (16.5% H_2O for $(CH_3)_4NOH \cdot 1H_2O$ and 37.2% H_2O for $(CH_3)_4NOH \cdot 3H_2O$); it is possible to obtain the monohydrate by removing the water at 35° under vacuum for 4 days. *Cf.* J. Walker and J. Johnston, *J. Chem. Soc.*, **87**, 958 (1905).

was then centrifuged and the viscosity was measured by conventional methods.

In order to be certain that the clean-up procedure did not affect any siloxane rearrangement, a separate experiment was carried out. A synthetic mixture containing 20% MM, 20% D_4, 20% decamethyltetrasiloxane (MD_2M) and 40% decamethylcyclopentasiloxane (D_5) was placed on an electric shaker with an equal volume of 3 *N* HCl for 20 hours. At the end of this time, the oil was washed with water until the washings had a *p*H of about 4. The washing was followed by drying over anhydrous sodium carbonate and finally by treatment with Celite-270. A portion of the sample was then subjected to analytical distillation in order to ascertain the composition of the resultant oil. The observed distillation data are presented in Table I.

TABLE I

COMPOSITION OF DISTILLATE OF M AND D COMPOUNDS AFTER CLEAN-UP PROCEDURE

Compound	Made-up, %	Found, %
MM	20	20.4, 20.6
MD_2M	20	22.2, 22.2
D_4	20	20.1, 19.1
D_5	40	37.6, 39.5

An examination of Table I clearly indicates that the amount of M and D compounds recovered by distillation is essentially the same as that put into the original mixture. It was further observed that the viscosity of a sample of a one-to-one molar mixture of MM and D_4 was the same before and after the clean-up procedure. Thus, it may be concluded that the clean-up procedure does not affect the properties of the siloxanes.

The results of the measurements of the viscosity of the solution as a function of time during the base-catalyzed equilibration of a one-to-one molar mixture of MM and D_4 with 0.1% tetramethylammonium hydroxide are presented in Table II. The densities of the various oil samples were determined with a Fischer–Davidson gravitometer which measures the density at 20° regardless of small variations in the ambient temperature. The densities at 25° were calculated by assuming a cubical thermal expansion coefficient of 0.001 as an average value for methylsilicones in agreement with the measurements of Hurd.[17] Viscosities were measured using Cannon viscometers at 25.00 ± 0.02°.

The summary of the data which are presented in Table II include data from three separate experiments. The data of Table II are presented in the graph of Fig. 1. It may be clearly seen that the viscosity passes through a maximum before returning to the same equilibrium value as found by Scott.[2]

In order to investigate the nature of the oil in the vicinity of the viscosity maximum, a separate experiment was carried out in which 300 g. of a one-to-one molar mixture of MM and D_4 was equilibrated with tetramethylammonium hydroxide at 80° to a viscosity of 8.86 cs. at 25.0°. This sample was cooled to room temperature, washed and filtered in the usual manner. Upon distillation, an aliquot of this sample yielded 62–64 g. of MM, a trace of MDM, 41 g. of D_4 and 72 g. of a relatively viscous non-distillable oil (b.p. > 180° at 1 mm.). The residual oil had a viscosity of 157 cs. at 25°. A cryoscopic determination of molecular weight of the residual oil (0.4610 g. of oil in 19.25 g. of anhydrous cyclohexane) gave a molecular weight of 5,460. The nature of the residual oil is an MD_xM type polymer in which x averages *ca.* 72. Thus, during the course of the equilibration a large amount of D_4 was consumed and only a small amount of MM was used up.

These data then indicate that the mechanism of the base-catalyzed equilibration of an M–D system involves the initial formation of only relatively high molecular weight material.

$$MM + x/4\, D_4 \xrightarrow[80^\circ]{0.1\%\ (CH_3)_4NOH} MD_xM (x \approx 72) \qquad (1)$$

TABLE II

VISCOSITY AS A FUNCTION OF TIME OF 1:1 MOLAR MIXTURES OF MM PLUS D_4 EQUILIBRATED AT 80° WITH 0.1% $(CH_3)_4NOH$

Time of equilibration, hr.	η_{25}(cs.)	$d^{20}{}_4$	$d^{25}{}_4$	η_{25}(cp.)
0	1.18	0.875	0.870	1.01
1	3.74	.891	.886	3.37
1	3.68	.883	.878	3.23
1	4.12	.882	.877	3.62
1.5	6.38	.884	.879	5.62
2	7.64	.885	.880	6.73
2	7.63	.887	.882	6.73
2.5	7.58	.885	.880	6.68
2.5	8.14	.887	.882	7.17
3	8.48	.898	.893	7.59
3	8.29	.887	.882	7.31
3	8.38	.888	.883	7.41
3.5	7.70	.887	.882	6.80
4	6.69	.900	.895	5.99
4	7.16	.889	.884	6.33
5	6.05	.890	.885	5.35
6	5.66	.888	.883	5.00
6.5	5.18	.887	.882	4.57
6.5	5.32	.899	.894	4.76
11	3.94	.894	.889	3.50
16	3.24	.888	.883	2.86
20	3.12	.889	.884	2.76
27	3.06	.890	.885	2.71
32	2.98	.890	.885	2.64
89	2.87	.889	.884	2.54
318	2.87	.890	.885	2.54

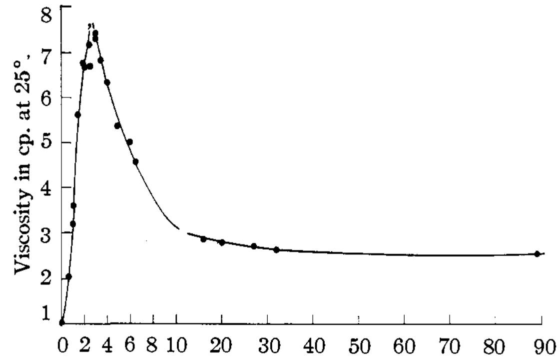

Fig. 1.—Viscosity *vs.* time for equilibration of one mole of MM and one mole of D_4 with 0.1% $(CH_3)_4NOH$ at 80°.

The relatively long linear molecules of the type MD_xM cause the high viscosity. Then the attainment of the equilibrium viscosity value of 2.51 centipoises,[1] should involve reactions of the type depicted by equations 2 and 3.

$$MD_xM + MM \longrightarrow MD_{x-1}M + MDM \qquad (2)$$

$$MD_xM + MDM \longrightarrow MD_{x-3}M + MD_4M \qquad (3)$$

It is obvious that a large variety of reactions of this type may occur. It is also to be observed that equations 2 and 3 and their prototypes involve no change in the number average molecular weight, while reactions of the type indicated in equation 1 do involve such a change. Therefore, measurements of number average molecular weight during equilibration should confirm this concept of the course of the reaction.

The number average molecular weights have been determined by a conventional cryoscopic method using cyclohexane (K_f = 20.0) as a solvent. Such measurements are often subject to errors due to association of the solute resulting in low apparent molecular weight values. A check of the number average molecular weight ($\bar{M}_n$) of an equimolar mixture of MM + D_4 gave a value of 223 (calcd. 229) in a solution 0.08 molal in each component. By operating

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[17] C. B. Hurd, THIS JOURNAL, 68, 364 (1946).

well below this concentration, errors due to association were negligible for the present purpose. These data are presented in Table III in which the equilibration time; the weight of solvent, w_1; the weight of solute, w_2; the freezing point depression, ΔT; and the number average molecular weight, M_n, are tabulated.

TABLE III

NUMBER AVERAGE MOLECULAR WEIGHT (M_n) AS A FUNCTION OF TIME FOR 1:1 MOLAR MIXTURE OF MM + D_4 EQUILIBRATED AT 80° WITH 0.1% $(CH_3)_4NOH$

Time of equilibration, hr.	w_1 (g. cyclohexane)	w_2 (g. solute)	ΔT (°C.)	M_n
1.0	19.25	0.3311	1.405	245
1.0	19.24	.3349	1.360	256
1.5	19.24	.3239	1.263	267
2.0	19.20	.3390	1.149	308
2.5	19.20	.3514	1.121	326
2.5	19.23	.3224	1.007	333
3.0	19.26	.3676	1.077	354
4.0	19.28	.3357	0.932	373
5.0	19.19	.3420	.927	385
16	19.25	.3234	.845	398
20	19.23	.3672	.913	419
27	19.21	.3388	.897	393
89	19.24	.3576	.848	438
Starting mixture MM + D_4	19.24	.7110	3.313	223 (calcd. 229)

These data are plotted in Fig. 2 from which it may be seen that the number average molecular weight increases rapidly during the period in which the equilibrating system is reaching a viscosity maximum. After this there is a gradual rise to the equilibrium value of M_n = 438 (*cf.* Table III), a value which is comparable to the value found by Scott[2] for the equilibrium solution, M_n = 438 ± 20. The authors estimate that an error of about ±20 is involved in the M_n values of Table III.

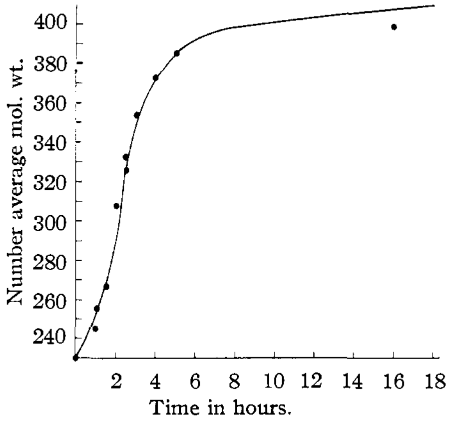

Fig. 2.—Number average molecular weight *vs.* reaction time at 80° for one mole of MM and 1 mole of D_4 with 0.1% $(CH_3)_4NOH$.

These data thus support the concept that reactions of the type of equation 1 predominate in the early stages of the reaction, then reactions of the type of equations 2 and 3 predominate in the later stages of the equilibration.

TABLE IV

CHANGES IN PHYSICAL PROPERTIES OF 1:1 MOLAR MM AND D_4 WITH $(CH_3)_4NOH$ AT 80°

Equilibration time, hr.	$n^{20}D$	d^{20}_4	R_D	$N(R_D)$	N (calcd.)
0	1.3889	0.875	0.2702	2.35	2.33
1	1.3913	.882	.2696	2.34	2.33
1.5	1.3929	.884	.2699	2.34	2.33
3	1.3947	.888	.2698	2.34	2.33
16	1.3948	.888	.2699	2.34	2.33
89	1.3950	.889	.2697	2.34	2.33
318	1.3950	.890	.2697	2.34	2.33
Non-distillable residues					
3[a]	1.4052	0.958	0.2560	2.08	2.03
6[a]	1.4049	.962	.2547	2.06	2.05
318[a]	1.4009	.932	.2606	2.17	2.17

[a] These three samples were non-distillable oils obtained by stripping the solutions after the indicated equilibration time.

Density and Refractive Index Relations.—During the course of base-catalyzed equilibration of MM and D_4 with tetramethylammonium hydroxide, the density and refractive index increase in a regular manner. Values of these properties are listed in Table IV. Other quantities in Table IV are the specific refraction $R_D = (n^2 - 1)/(n^2 + 2) \times 1/d$ and $N(R_D)$ which is the ratio of methyl groups to silicon atoms in the siloxane sample as calculated by the method of Sauer.[18] N(calcd.) is the ratio of methyl groups to silicon atoms in the siloxane mixture calculated from the known composition of the mixture. The cryoscopic molecular weights of the three non-distillable residues were 5460, 3210, 856 corresponding to $MD_{72}M$, $MD_{42}M$, and $MD_{9.4}M$, respectively. N(calcd.) values of Table IV have been derived from these molecular weights. The general agreement of N (calcd.) with $N(R_D)$ in these cases is further evidence that these samples consist of mixed MD_xM molecules. Errors in $N(R_D)$ could be reduced by more careful density measurements. Nevertheless, the $N(R_D)$ values of all the unfractionated samples are the same indicating that no major loss of volatile M compounds occurs during the equilibration and sampling. The density values of Table IV are plotted as a function of time in Fig. 3.

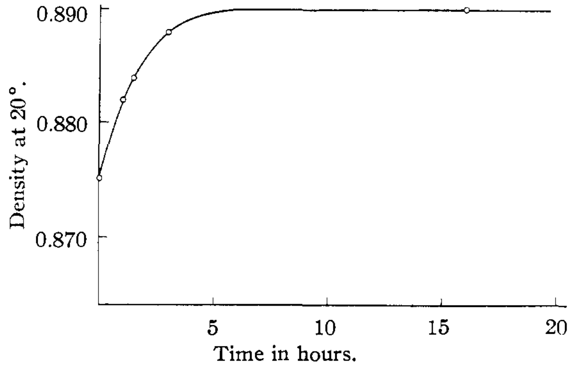

Fig. 3.—Density *vs.* time for base-catalyzed equilibration of one mole of MM and one mole of D_4 at 80° (0.1% $(CH_3)_4NOH$).

A sample of one-to-one molar MM and D_4 was equilibrated at 80° with 0.1% tetramethylammonium hydroxide

TABLE V

ANALYTICAL DISTILLATION DATA FOR A 1:1 MOLAR MM AND D_4 SOLUTION EQUILIBRATED WITH 0.1% TETRAMETHYL AMMONIUM HYDROXIDE

Compound	Found, wt., %	Calcd. by Scott,[2] wt., %	Compound	Found, wt., %	Calcd. by Scott,[2] wt., %
MM	8.6	7.6	D_5	1.3	1.4
MDM	8.2	8.7	MD_4M	8.3	8.2
D_4	3.3	3.6	MD_5M	7.1[a]	7.4
MD_2M	8.8	9.0	Residue	39.6	38.5[b]
MD_3M	8.0	8.7			

[a] This value was estimated from analysis of a three component mixture. [b] The Experimental value found by Scott[2] in acid equilibration.

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[18] R. O. Sauer, THIS JOURNAL, 68, 960 (1946).

for a sufficient time to ensure the attainment of equilibrium. An aliquot was then subjected to analytical distillation. The data obtained in this fashion are presented in Table V along with the calculated values as determined by Scott[2] for this system.

Since the viscosity, refractive index, density and composition of the equilibrium solution from the base-catalyzed equilibrations of one-to-one molar solutions of MM and D_4 are identical with those reported by Scott[2] for the case of acid-catalyzed equilibration, one must conclude that the same equilibrium state is reached independent of the type of catalyst employed.

In order to be certain that a viscosity maximum did not occur during the course of the sulfuric acid-catalyzed equilibration of MM and D_4, an experiment was set up at room temperature in which 500 g. of 1:1 molar mixture of MM and D_4 was equilibrated with 4% sulfuric acid (96% H_2SO_4). During the course of equilibration, samples were withdrawn at various times, washed and dried, after which the viscosity was measured. In Table VI these data are presented. The centistoke viscosity, the density of 25°, the centipose viscosity and the reaction time are presented in Table VI.

TABLE VI

VISCOSITY AS A FUNCTION OF TIME DURING SULFURIC ACID EQUILIBRATION

Time, hr.	η_{25} (cp.)	$d^{25}{}_4$	η_{25} (cp.)
0	1.18	0.870	1.01
1	1.44	.878	1.27
2	1.62	.878	1.42
3	1.80	.880	1.58
5	2.16	.882	1.91
8	2.53	.882	2.23
14	2.80	.883	2.47
24	2.84	.885	2.51
32.3	2.85	.886	2.51
72	2.85	.883	2.51

The data of this table are plotted in Fig. 4. An examination of Fig. 4 clearly shows that there is no maximum in the viscosity *vs.* time curve, and as a result one must conclude that base-catalyzed equilibration proceeds by means of a mechanism quite different from that involved in acid-catalyzed equilibration of siloxanes.

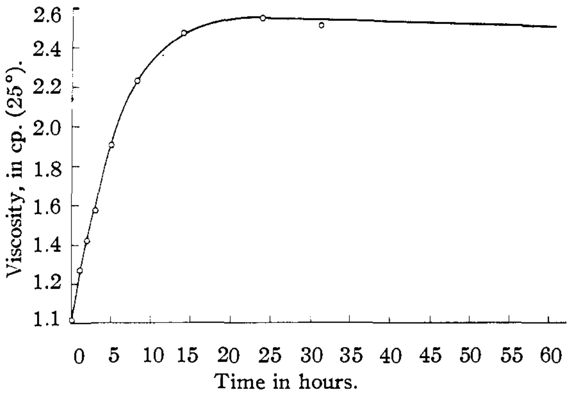

Fig. 4.—Viscosity *vs.* time of reaction for equilibration of one mole of MM and one mole of D_4 with 4% H_2SO_4 at room temperature.

Equilibration of MDM and D_4 with Tetramethylammonium Hydroxide at 80.0°.—The data for the equilibration of one mole of MDM and 0.75 mole of D_4 with 0.1% tetramethylammonium hydroxide at 80° are presented in Table VII. The quantities of MDM and D_4 were chosen in order to maintain the M/D ratio, α,[19] at 0.5 which is the same as in the case of the experiments with MM and D_4. In Table VII are presented the centistoke viscosity at 25°, η_{25}(cs.); the densities at 20 and 25°, $d^{20}{}_4$ and $d^{25}{}_4$, respectively; the centipoise viscosity at 25°, η_{25}(cp.); and the refractive index at 20°, $n^{20}{}_D$; all as a function of the time of equilibration.

TABLE VII

BASE-CATALYZED EQUILIBRATION OF 1 MOLE MDM AND 0.75 MOLE D_4 WITH 0.1% $(CH_3)_4NOH$ AT 80°

α(M to D ratio) = 0.5

Time, hr.	η_{25}(cs.)	$d^{20}{}_4$	$d^{25}{}_4$	η_{25}(cp.)	$n^{20}{}_D$
0	1.375	0.879	0.874	1.205	1.3892
1	2.18	.885	.880	1.92	1.3919
2	2.75	.886	.881	2.43	1.3931
3	2.87	.887	.882	2.53	1.3937
4	2.88	.887	.882	2.54	1.3939
5	2.83	.889	.884	2.50	1.3940
6	2.85	.889	.884	2.52	1.3941
7	2.83	.891	.886	2.51	1.3942
24	2.82	.890	.885	2.50	1.3948
96	2.84	.890	.885	2.51	1.3950

The viscosity *vs.* time data are plotted in Fig. 5. It will be observed that only a small maximum in viscosity occurs in this case. It should also be observed that while the final viscosity of 2.51 centipoise at 25° was attained in five to six hours, the density and refractive index continue to change for the first 24 hours. This behavior is indicative of the fact that the equilibration reaction is proceeding in spite of the fact that no change of viscosity may be observed.

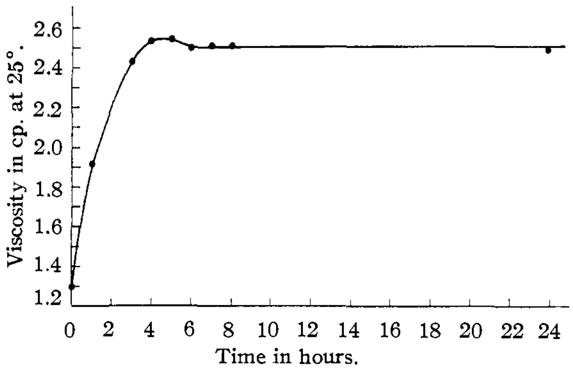

Fig. 5.—Viscosity *vs.* time for equilibration of MDM and D_4 with 0.1% $(CH_3)_4NOH$ at 80° ($[MDM]/[D_4] = 1.33$ or $\alpha = 0.5$).

The number average molecular weights, M_n, of the various samples were determined cryoscopically in anhydrous cyclohexane. These data are recorded in Table VIII as a function of the equilibration time.

TABLE VIII

NUMBER AVERAGE MOLECULAR WEIGHT AS A FUNCTION OF EQUILIBRATION TIME FOR THE SYSTEM MDM-D_4 WITH 0.1% $(CH_3)_4NOH$ ($\alpha = 0.5$)

Equilibration time, hr.	M_n	Equilibration time, hr.	M_n
0	229	4	409
1	312	6	419
2	372	7	404
3	393	24	426

The data of Table VIII are presented in Fig. 6. The same general type of molecular weight against time relation is observed as in the case of MM and D_4. This substantiates the concept that the same type of mechanism is operative in this case as in the case of the base-catalyzed equilibration of MM and D_4.

Equilibration of MD_2M and D_4 with Tetramethylammonium Hydroxide at 80.0°.—The data for the equilibration of one mole of MD_2M and 0.5 mole of D_4 with 0.1% tetramethylammonium hydroxide at 80.0° are presented in

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[19] The use of α has been employed advantageously by W. I. Patnode and J. R. Elliott, previously unpublished data, 1944.

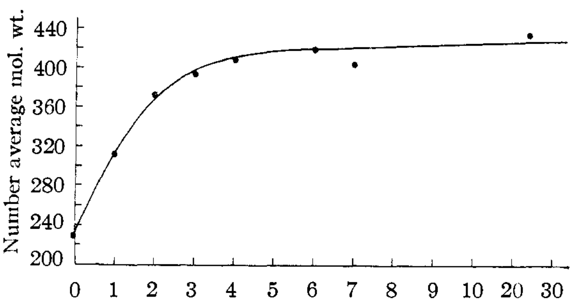

Fig. 6.—Number average molecular weight *vs.* equilibration time for the system MDM and D_4 with 0.1% $(CH_3)_4NOH$ at 80° ($[MDM]/[D_4]$ = 1.33 or α = 0.5).

Table IX. Again it should be observed that the quantities of MD_2M and D_4 were chosen so that α = 0.5 as in the case of the other equilibration experiments. The data for a duplicate run are presented at the bottom of Table IX and it will be seen that the agreement is within 3%.

Table IX

Base-catalyzed Equilibration of 1 Mole of MD_2M and 0.5 Mole D_4 with 0.1% $(CH_3)_4NOH$ at 80°

α(M to D ratio) = 0.5

Equilibration time, hr.	η_{25}(cs.)	d^{20}_4	d^{25}_4	η_{25}(cp.)	$n^{20}D$
		Run A			
0	1.67	0.882	0.877	1.47	1.3908
1	2.20	.887	.882	1.94	1.3932
2	2.60	.887	.882	2.29	1.3935
3	2.73	.887	.882	2.41	1.3940
4	2.77	.888	.883	2.44	1.3946
5	2.78	.888	.883	2.45	1.3947
6	2.78	.889	.884	2.46	1.3948
24	2.83	.889	.884	2.51	1.3950
48	2.93	.889	.884	2.58	1.3950
118	2.86	.888	.883	2.53	....
		Duplicate Run B			
1	2.20	0.886	0.881	1.94	....
2	2.54	.886	.881	2.24	....
3	2.70	.887	.882	2.39	....
4	2.75	.887	.882	2.42	....
6	2.78	.888	.883	2.45	....

The viscosity *vs.* time data of Table IX are plotted in the graph of Fig. 7. It will be seen that no viscosity maximum occurred in this case. However, the same equilibrium composition as found with an acid catalyst was again obtained. This was shown by distillation of an equilibrium solution which was equilibrated at 80.0° for 118 hours. The distillation data are presented in Table X.

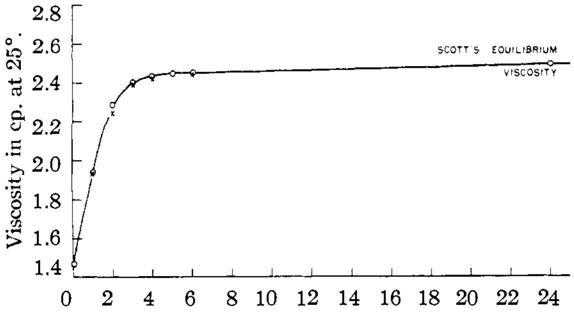

Fig. 7.—Viscosity *vs.* time for the equilibration of MD_2M and D_4 at 80° with 0.1% $(CH_3)_4NOH$ ($[MD_2M]/[D_4]$ = 2.0 or α = 0.5).

Table X

Distillation Data from the Equilibrium Solution Obtained from the Equilibration of One Mole of MD_2M and 0.5 Mole D_4 with 0.1% $(CH_3)_4NOH$ at 80.0°

Compound	Found, wt., %	Calcd. by Scott, wt., %	Compound	Found, wt., %	Calcd. by Scott, wt., %
MM	5.6	7.6	MD_3M	6.1	8.7
MDM	8.6	8.7	MD_4M	7.3	8.2
D_4	2.4	3.6	MD_5M	6.2	7.4
MD_2M	10.5	9.0	MD_6M	6.9	6.6
D_5	2.0	1.4	MD_7M	6.5	..

In order to show that the equilibration of MD_2M and D_4 followed the same type of mechanism as proposed for the equilibration of MM and D_4 (*cf.* equations 1–3), a mixture of one mole of MD_2M and 0.5 mole D_4 was equilibrated with 0.1% tetramethylammonium hydroxide at 80° for one hour, worked up and retained in its entirety for distillation. The data of the analytical distillation of this sample are presented in Table XI.

Table XI

Analytical Distillation of Sample of MD_2M and D_4 (α = 0.5) after One Hour Equilibration at 80° with 0.1% Tetramethylammonium Hydroxide

Compound	Wt., %	Compound	Wt., %
MM	Trace	D_5	11.1
MDM	2	MD_3M-MD_6M	
D_4	11.0	Residue	18.7
MD_2M	57		

The original composition of this sample before equilibration was 67.8 wt. % MD_2M and 32.2 wt. % D_4. The percentages of MD_2M and D_4 left after one hour of equilibration indicate that D_4 is more reactive toward bases than MD_2M. The residue (b.p. >178° at 10 mm.) had a number average molecular weight of 1110; this was determined with a solution of 0.3546 g. of residue in 19.24 g. of cyclohexane (ΔT_f = 0.333°). This value of M_n = 1110 corresponds to a siloxane having the average composition of $MD_{12.8}M$.

The Equilibration of MD_2M and D_4 at a Small Value of α = 0.0464.—The data for the equilibration of 0.0973 mole of MD_2M and one mole of D_4 (α = 0.0464) with 0.1% tetramethylammonium hydroxide at 80° are presented in Table XII. The viscosities as a function of time are plotted in Fig. 8. The values from two separate experiments generally agreed within a few per cent. The final equilibrium value of the viscosity was 41.7 cs. at 25°. The viscosity

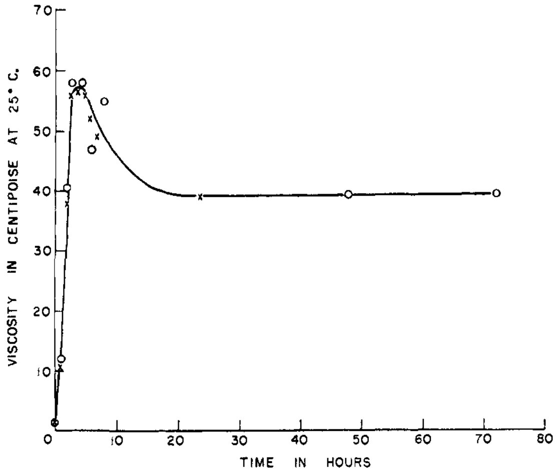

Fig. 8.—Viscosity *vs.* time for equilibration of 0.0973 mole of MD_2M and one mole of D_4 with 0.1% $(CH_3)_4NOH$ at 80°; O, run A; ×, run B.

of the equilibrium sample was also measured as 35.6 cs. at 100°F. This value agrees fairly well with the 34.5 cs. expected for a system where $\alpha = 0.0464$.[20]

A maximum in the viscosity *vs.* time relationship was obtained for this system ($\alpha = 0.0464$) whereas no maximum was obtained with the same two siloxanes when $\alpha = 0.5$. The large mole fraction of D_4 is responsible for this maximum since at increased concentration the rate of reaction of D_4 exceeds that of MD_2M leading to a maximum in the viscosity *vs.* time relation. The usual physical properties are listed in Table XII for two separate runs.

TABLE XII

BASE-CATALYZED EQUILIBRATION OF 0.0973 MOLE MD_2M AND 1 MOLE D_4 WITH 0.1% $(CH_3)_4NOH$ AT 80°

α(M to D Ratio) = 0.0464

Time, hr.	η_{25}(cs.)	d^{20}_4	d^{25}_4	η_{25}(cp.)	$n^{20}D$
0	2.18	0.945	0.940	2.05	1.3959
0	2.185	.944	.939	2.05	1.3960
1	12.7	.946	.941	11.9	1.3984
1	11.7	.945	.940	11.0	1.3984
2	43.0	.946	.941	40.5	1.4011
2	40.3	.948	.943	38.0	1.4010
3	61.8	.942	.937	57.9	1.4025
3	59.2	.949	.944	55.9	1.4028
4	59.9	.950	.945	56.6	1.4032
4.5	61.3	.948	.943	57.8	1.4033
5	59.0	.950	.945	55.8	1.4034
6	49.7	.949	.944	46.9	1.4037
6	55.1	.950	.945	52.1	1.4035
7	51.6	.950	.945	48.8	1.4035
8	58.4	.947	.942	55.0	1.4037
24	41.4	.950	.945	39.2	1.4036
48	41.6	.951	.946	39.4	1.4038
72	41.8	.951	.946	39.5	1.4037
167	41.8	.950	.945	39.5	1.4037
330	41.7	.951	.946	39.5	1.4031

The Base-catalyzed Equilibration of MM and D_3.—The data for the equilibration of 1 mole MM and 1.33 moles D_3 ($\alpha = 0.5$) with 0.1% tetramethylammonium hydroxide at 80° are presented in Table XIII. The viscosities as a function of time are plotted in Fig. 9. The extremely large viscosity maximum obtained in this case is indicative of the great reactivity of hexamethylcyclotrisiloxane toward bases. After 168 hours the reaction had reached the equilibrium state for this system ($\alpha = 0.5$) and the viscosity had decreased 2.53 cp.

TABLE XIII

BASE-CATALYZED EQUILIBRATION OF 1 MOLE MM AND 1.33 MOLES D_3 WITH 0.1% $(CH_3)_4NOH$ AT 80°

α(M to D ratio) = 0.5

Time, hr.	η_{25}(cs.)	d^{20}_4	d^{25}_4	η_{25}(cp.)
0[a]	...	...	...	...
0.5	110.8	0.813	0.808	89.6
1	26.4	.877	.872	22.8
2	20.0	.884	.879	17.6
3	9.74	.895	.890	8.66
4	7.30	.899	.894	6.53
6	5.42	.902	.897	4.86
23	3.74	.895	.890	3.33
72	3.36	.884	.879	2.95
168[b]	2.86	.888	.883	2.53

[a] Since D_3 (1.33 moles) was not completely soluble in the MM (1 mole) at 25°, the viscosity data could not be obtained; at 80°, D_3 dissolved completely to give a homogeneous solution. [b] $n^{20}D$ 1.3949.

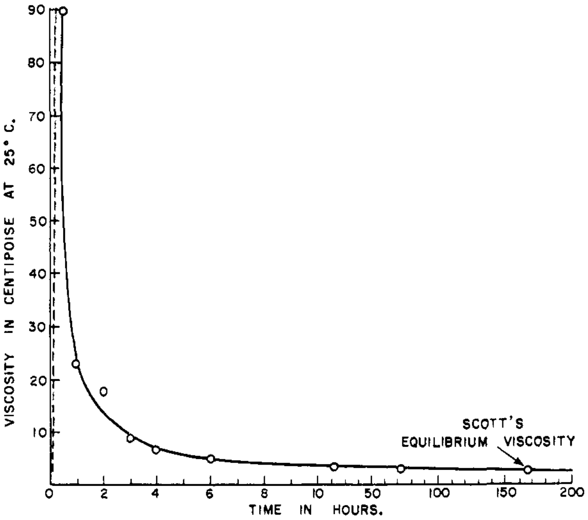

Fig. 9.—Viscosity *vs.* time for equilibration of MM and D_4 with 0.1% $(CH_3)_4NOH$ at 80° ($[MM]/[D_3] = 0.75$ or $\alpha = 0.5$).

The Acid-catalyzed Equilibration of MM and D_3.—The data for the acid-catalyzed equilibration of one mole of MM and 0.55 mole of D_3 are presented in Table XIV. The usual properties are given.

TABLE XIV

DATA FOR THE ACID-CATALYZED EQUILIBRATION OF ONE MOLE OF MM AND 0.55 MOLE OF D_3 WITH 4% H_2SO_4 AT ROOM TEMPERATURE

Time of equilibration, hr.	η_{25}(cs.)	d^{20}_4	d^{25}_4	η_{25}(cp.)	$n^{20}D$
0[a] —	0.72	0.825	0.820	0.59	1.3808
0.167[b]	1.49	.844	.839	1.26	1.3891
0.5	1.66	.845	.840	1.40	1.3893
1	1.54	.844	.839	1.30	1.3892
1.5	1.51	.844	.839	1.27	1.3891
2	1.47	.844	.839	1.24	1.3890
2.5	1.45	.844	.839	1.22	1.3890
3	1.42	.844	.839	1.20	1.3890
4	1.40	.844	.839	1.18	1.3890
5	1.40	.844	.839	1.18	1.3890
72	1.40	.844	.839	1.18	1.3890

[a] Represents the initial mixture prior to the addition of the catalyst. [b] Weighed out 24 g. of hexamethyldisiloxane and 18 g. of D_3 and equilibrated this mixture with 0.93 cc. (4% by weight) of H_2SO_4. After 10 minutes of equilibrating a sample was withdrawn and gave the above results. The purpose was to see if a maximum viscosity had been reached prior to the one-half hour sample withdrawn from the original mixture.

The viscosity–time relation for this system is presented

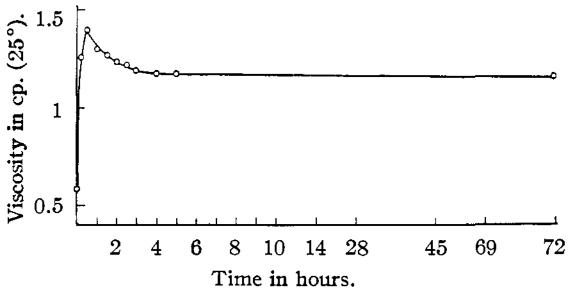

Fig. 10.—Viscosity at 25° *vs.* equilibration time of MM and D_3 with 4% H_2SO_4 at room temperature ($[MM]/[D_3] = 1.82$ or $\alpha = 1.21$).

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(20) This equilibrium viscosity value was obtained from a plot of log α *vs.* log viscosity at 100°F.; reference 19.

in Fig. 10. The very great reactivity of D_3 toward acids was considered to be the cause of the viscosity maximum. In this case it was assumed that the mechanism of the reaction involved steps similar to those in the case of the base-catalyzed equilibration of MM and D_4. Of course, it should be recognized that the attack of acidic and basic catalysts on the siloxanes differ greatly.

Acid-catalyzed Equilibration of MD_2M and D_4.—A study of the equilibration (by sulfuric acid) of the system MD_2M and D_4 with $\alpha = 0.5$ was carried out to determine whether or not a viscosity maximum occurs. That such is not the case may be seen by an examination of the data of Table XV.

TABLE XV

DATA FOR THE ACID-CATALYZED EQUILIBRATION OF ONE MOLE OF MD_2M WITH 0.5 MOLE OF D_4 WITH 4% H_2SO_4 ($\alpha = 0.5$) AT ROOM TEMPERATURE

Time of equilibration, hr.	η_{25}(cs.)	$d^{20}{}_4$	$d^{25}{}_4$	η_{25}(cp.)	$n^{20}{}_D$
0^a	1.66	0.884	0.879	1.47	1.3918
1	2.57	.888	.883	2.28	1.3942
2	2.76	.889	.884	2.45	1.3948
3	2.82	.889	.884	2.51	1.3949
4	2.83	.889	.884	2.52	1.3949
5	2.83	.890	.885	2.52	1.3949
6	2.83	.890	.885	2.52	1.3950
7	2.83	.890	.885	2.52	1.3950
24	2.83	.890	.885	2.52	1.3950
30	2.84	.890	.885	2.53	1.3950
48	2.83	.890	.885	2.52	1.3950

[a] Represents the initial mixture before the addition of the catalyst.

The data of Table XV are presented in Fig. 11, from which it will be seen that the viscosity increases in a regular manner during the equilibration.

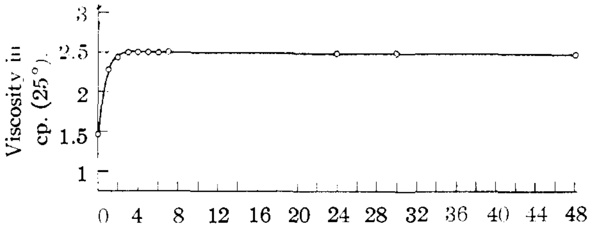


Fig. 11.—Viscosity in centipoise (25°) *vs.* time in hours for equilibration of one mole of MD_2M with 0.5 mole D_4 (α = 0.5) at room temperature with 4% sulfuric acid as catalyst.

Discussion

One may write the following general reactions (some of which may be complex) which contribute principally to the over-all base-catalyzed equilibration of MM and D_4.

$$-D_x- + D_4 \xrightarrow{k_1} -D_{x+4}- \qquad (4)$$

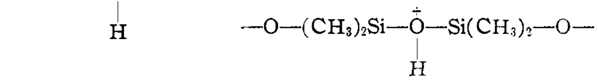
$$-D_x- + MM \xrightarrow{k_2} MD_xM \qquad (5)$$

$$MD_xM + MM \longrightarrow MD_{x-z}M + MD_zM \qquad (6)$$

$$MD_xM + MD_yM \longrightarrow MD_{x+w}M + MD_{y-w}M \qquad (7)$$

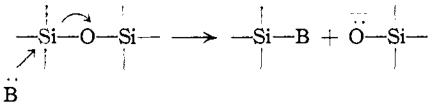
Reactions 4 and 5 cause an increase in number average molecular weight of the system while reactions 6 and 7 produce no change in the number of molecules in the system and therefore do not affect the number average molecular weight as observed previously. Referring to Fig. 2, it will be observed that $\bar{M}_n$ increases rapidly during the first few hours, indicating that reactions 4 and/or 5 are proceeding rapidly. However, the large viscosity increase in this time interval (Fig. 1) strongly suggests that reaction 4 predominates initially, when the monomers MM and D_4, are at equal molar concentrations. In other words, $k_1 >> k_2$. Rapid depletion of D_4 soon leads to a relatively larger amount of reaction 5. Later a viscosity decrease takes place accompanied by little change in $\bar{M}_n$, indicating that reactions 6 and 7 are responsible for the attainment of the final equilibrium.

From the results of these experiments, it is clear that the equilibrium state of M and D siloxane systems is dependent on the molar ratio of M to D units and not on the types of siloxanes used in equilibration. This conclusion is correct whether an acid or a base catalyst is used. The type of catalyst used markedly changes the path to equilibrium but not the end state. A study of the methanolysis of siloxanes has previously demonstrated that hexamethyldisiloxane is more reactive than octamethylcyclotetrasiloxane in the presence of an acid catalyst.[21] This order of reactivity would lead to the result obtained with the sulfuric acid equilibration of MM and D_4 where no maximum is obtained. Presumably the reactions with acid catalysts involve protonated species such as



$$(CH_3)_3Si-\underset{H}{\overset{+}{O}}-Si(CH_3)_3 \quad \text{and} \quad -O-(CH_3)_2Si-\underset{H}{\overset{+}{O}}-Si(CH_3)_2-O-$$

The fact that a D unit is more reactive than an M unit toward a base (thereby causing a viscosity maximum) is in complete agreement with the mechanism of the reaction of siloxanes with bases postulated by Hurd, Osthoff and Corrin.[22] These authors proposed that the attack of a base on a siloxane takes place at the silicon atom with a displacement of the siloxanyl bond, thus



Indeed, the electronegativity of the oxygen atoms create a larger positive charge on the silicon atom in a D unit than in an M unit and a base would be expected to cleave a D–D bond more readily than an M–M bond.

From the results of equilibration of various D and M containing siloxanes it is possible qualitatively to assign the following decreasing order of reactivity of siloxanes toward bases: $D_3 > D_4 > MD_2M > MDM > MM$.

On the other hand, the methanolysis of siloxanes with an acid catalyst, has demonstrated the following decreasing order of reactivity[21]

$$D_3 > MM > MDM > MD_2M > D_4$$

The acid-catalyzed equilibrations of M and D units described in the present paper confirm this order of reactivity.

Acknowledgment.—The authors express their appreciation to E. M. Hadsell for his coöperation and assistance in the many distillations which he

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[21] W. T. Grubb, THIS JOURNAL, **76**, 3408 (1954).

[22] D. T. Hurd, R. C. Osthoff and M. L. Corrin, *ibid.*, **76**, 249 (1954).

carried out during the course of this study and to John Keil, who determined some of the physical properties reported in this paper.

SCHENECTADY, NEW YORK

[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY, THE OHIO STATE UNIVERSITY]

The Vapor Phase Photolysis of Trifluoroacetone at Wave Length 3130 Å.[1]

BY ROBERT A. SIEGER AND JACK G. CALVERT[2]

RECEIVED JUNE 5, 1954

A kinetic study is made of the photolysis of CF_3COCH_3 vapor at various temperatures, concentrations, and light intensities to determine the relative reactivity of CF_3 and CH_3 toward H-abstraction reactions. The gaseous products are: CO, CH_4, CF_3H, C_2H_6, CF_3CH_3 and C_2F_6. In experiments at low $[CF_3COCH_3]$ and high I_a the methanes and ethanes are formed only in the reactions: $CH_3 + CF_3COCH_3 \rightarrow CH_4 + CF_3COCH_2$ (1); $2CH_3 \rightarrow C_2H_6$ (2); $CF_3 + CF_3COCH_3 \rightarrow CF_3H + CF_3COCH_2$ (3); $2CF_3 \rightarrow C_2F_6$ (4). The activation energy differences are: $E_1 - E_2/2 = 8.9$; $E_3 - E_4/2 = 6.6$ kcal./mole; the Arrhenius P factors are: $P_1/P_2^{1/2} = 5 \times 10^{-4}$, $P_3/P_4^{1/2} = 1 \times 10^{-4}$. The quantum yields of CO, CH_4 and C_2H_6 are greater than 1.0 at high temperatures and increase markedly with temperature increase. The quantum yields of CF_3H, C_2F_6 and CF_3CH_3 are less than 1.0 at all temperatures and decrease at high temperatures. In explanation of these unusual results a chain mechanism is proposed which involves C_2H_6 formation in a reaction other than (2) at high temperatures. This may be a rare example of a methyl-abstraction reaction. The results provide evidence for a rarely postulated, gas phase, radical addition to a carbonyl double bond. It is suggested that CF_3 radicals generate CH_3 radicals at high temperatures by the reactions: $CF_3 + CF_3COCH_3 \rightleftarrows (CF_3)_2COCH_3$, and $(CF_3)_2COCH_3 \rightarrow CH_3 + CF_3COCF_3$.

In view of the results of the many detailed studies of acetone photolysis[3] it seemed probable that trifluoroacetone would undergo photodecomposition forming in part methyl and trifluoromethyl radicals. The present study was initiated in an attempt to gain information concerning the relative reactivity of the CH_3 and CF_3 radicals and to determine the effect of fluorine atom substitution in the acetone molecule on the mechanism of acetone photodecomposition.

Experimental

Apparatus.—The all-glass photolysis system consisted of a quartz photolysis cell (50 mm. long, 30 mm. diam.), a glass circulating pump, trap and mercury manometer. This system was isolated from stopcocks by mercury valves. The cell was suspended in an aluminum block furnace (regulated to ±1°). Radiation from a Hanovia type A(S-500) burner (run on a regulated 3.00 amp. a.c. current) was filtered to isolate wave length 3130 Å.[4] The light beam was well collimated by a series of lenses and stops so that a fairly homogeneous beam of radiation filled the cell volume (35.3 cc.) almost completely. The geometrical arrangement of all components in the light train remained fixed during the entire study. A photomultiplier-amplifier system was used to measure the fractions of light absorbed. Absolute intensities were estimated by chemical actinometry at five regularly spaced intervals during the course of the photochemical runs. Estimates of the total quanta entering the cell per sec. $\times 10^{-15}$ were: 1.14, 0.93 (uranyl oxalate actinometry[5]), 1.06, 1.19, 1.14 ($K_3Fe(C_2O_4)_3$ actinometry[6]). No aging of the light source was apparent, so an average value of 1.09×10^{15} q./sec. was used as the incident light intensity in quantum yield calculations for all runs. Calibrated uniform density filters were placed in the light path to obtain lower incident intensities in some experiments.

Materials.—Carefully fractionated CF_3COCH_3 was purchased from the Caribou Chemical Co. (b.p. 21-22° (750 mm.)) and further purified by fractionation at reduced pressure in a high vacuum system. The mass spectrum of the purified sample was consistent with that expected for pure CF_3COCH_3; approx. mol. wt. (Dumas method), 114 g./mole; approx. v.p. in mm., 6 (−65°), 18 (−51°), 98 (−23°), 200 (−9°), 385 (5°), 537 (12°). High purity reference samples of the gases CF_3H, C_2F_6, CH_3CF_3 and CF_4 were provided by the Organic Chemicals Department of E. I. du Pont de Nemours & Co. Additional samples of these gases were supplied by the Minnesota Mining and Manufacturing Co. and Professor J. D. Park, University of Colorado. C_2H_6 and CH_4 reference gases were Phillips Research Grade. CO was prepared by the action of H_2SO_4 on NaO_2CH and purified in the conventional manner.

Product Analysis.—A maximum of 2% photodecomposition of the original ketone was allowed in all runs. CO and CH_4 products were removed following photolysis using a Toepler pump with the other products and excess ketone condensed at liquid N_2 temperature. A second fraction of the products was removed from the ketone excess using a modified Ward still[7] maintained at −110 to −100°. The analysis scheme was checked with known mixtures; almost complete recovery of CH_4, CO, C_2F_6, C_2H_6, CF_3H and about 90% recovery of CF_3CH_3 could be effected from the excess ketone. (CF_3CH_3 is the product with the lowest vapor pressure.) CO was analyzed by chemical means[8] using a Blacet–Leighton gas analysis system. The ethanes and methanes were determined using a General Electric analytical mass spectrometer.

Results

Products.—CO, CH_4, C_2H_6, CH_3CF_3 and C_2F_6 were identified as the major gaseous products. Proved absent were the possible products CH_3F, CF_4, HF, SiF_4 and F_2. An unsuccessful attempt was made to identify other products from the mass spectrum of the condensable fraction containing excess ketone.

Molar Extinction Coefficients.—At a fixed temperature the absorption of 3130 Å. radiation by CF_3COCH_3 vapor followed Beer's law within the experimental error of the determinations over the range of concentrations, 17.3 to 0.84×10^{18} molec./cc. The coefficient showed an almost linear increase with increase in temperature. Representative values of ϵ for CF_3COCH_3 vapor at 3130 Å. are: 3.6 (25°) and 6.4 (350°), where $\log_{10}(I_0/I) =$

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(1) Taken from the thesis of R. A. Sieger submitted for the Master of Science degree, The Ohio State University, 1954. Presented in part before the Division of Physical and Inorganic Chemistry of the American Chemical Society, New York, September, 1954.

(2) Author to whom communications should be addressed.

(3) For reviews of work see: (a) W. Davis, Jr., *Chem. Revs.*, **40**, 201 (1947); (b) W. A. Noyes, Jr., and L. M. Dorfman, *J. Chem. Phys.*, **16**, 788 (1948).

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(5) W. G. Leighton and G. S. Forbes, *ibid.*, **52**, 3139 (1930); G. S. Forbes and L. J. Heidt, *ibid.*, **56**, 2363 (1934).

(6) C. A. Parker, *Proc. Roy. Soc.* (*London*), **A220**, 104 (1953).

(7) E. C. Ward, *Ind. Eng. Chem.*, *Anal. Ed.*, **10**, 169 (1938).

(8) F. E. Blacet, G. D. MacDonald and P. A. Leighton, *ibid.*, **5**, 272 (1933).