TABLE I

HYDROLYSIS RATE CONSTANTS

T, °C.	CH_3Cl		CH_2FCl		CHF_2Cl	
	k_2	$k_1 \times 10^5$	k_2	$k_1 \times 10^5$	k_2	$k_1 \times 10^6$
60	0.817	0.25	..	...	..	...
80	1.04	2.08	0.71	0.35	..	...
90	..	...	.79	1.01	..	...
100	1.26	10.9	.87	2.67	..	...
110	1.38	25.9	.94	5.36	..	...
120	1.49	46.5	1.02	12.0	4.89	1.16
130	...	...	1.10	25.2	5.27	2.40
140	...	...	1.18	49.0	5.65	5.55
150	...	...	..	...	6.04	9.5
160	...	...	..	...	6.42	18.5
170	...	...	..	...	6.80	26.6
180	...	...	..	...	7.18	42.2

mately 21 kcal./mole at the higher temperatures to about 23 kcal./mole at the lower.

A careful study of the hydrolysis of CH_3Cl by Moelwyn-Hughes[7] has given a rate constant of 1.08×10^{-4} and an activation energy of 22.7 kcal./mole, both at 100°, compared with the present values of 1.09×10^{-4} and 21.5 kcal./mole.

There is a steady decrease in the rate of hydrolysis of the chlorine atom in the compounds we have studied as the number of fluorine atoms attached to the same carbon increases. The energy of activation, however, is approximately the same for all of the substances, so that the difference is in the pre-exponential factor in the rate equation. In this connection, it is of interest to note that Glew and Moelwyn-Hughes[9] found that the hydrolysis rates of CH_3F and CH_3Br at 100° differed by a factor of 3,400, although their energies of activation were 21,163 and 21,424, respectively.

The solubility of a methyl halide gas is at least partially a measure of the forces of interaction between the methyl halide molecules and water molecules. The water solubility of the series CH_3F, CH_3Cl and CH_3Br rises[10] in a manner roughly parallel to the increase in rate of hydrolysis.[9] No such parallelism is noted in the series CH_3Cl, CH_2FCl and CHF_2Cl, however. In the temperature range we have used, CH_2FCl is more soluble than either of the other gases, but its hydrolysis rate is intermediate between the other two.

A few experiments on the rate of the reaction of CH_3Cl, CH_2FCl and CHF_2Cl with thiosulfate ion in dioxane–water solution show behavior very similar to that observed in the neutral hydrolysis reaction.[11] At 50.3°, the rate of the reaction between thiosulfate ion and CH_2FCl is slower than the reaction with CH_3Cl by a factor of about 15. CHF_2Cl reacts still more slowly than does CH_2FCl.

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(10) D. N. Glew and E. A. Moelwyn-Hughes, *Discussions Faraday Soc.*, **15**, 150 (1953).

(11) The experiments on the thiosulfate ion were performed by Mrs. Janice Goodwin Lonadier to whom the authors are indebted.

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY, SCHENECTADY, NEW YORK]

Radiation Chemistry of Polydimethylsiloxane.[1] I. Crosslinking and Gas Yields

BY A. A. MILLER

RECEIVED NOVEMBER 30, 1959

The electron-irradiation of a linear polydimethylsiloxane oil, $[-Si(CH_3)_2O-]_n$, with a molecular weight of 85,000, was studied in the glass state at −180° and in the fluid state from −40 to +150°. At 25° and a radiation intensity of 13.8×10^6 r./min., the crosslinking yield, derived from gel and gas measurements, is G(c.l.) = 3.0. In the fluid state the crosslink and gas yields are both temperature- and intensity-dependent. The transition from the fluid to the glass state produces some apparent anomalies in the over-all radiation chemical effects.

Introduction

A review of the earlier literature on the effects of ionizing radiation in silicone polymers has been compiled by Bovey.[2] Thus far, no systematic study of the radiation chemistry of the linear polydimethylsiloxane $[-Si(CH_3)_2O-]_n$ structure has been reported. Kantor has reported work on the cyclic tetramer[3] and Dewhurst and St. Pierre have studied the irradiation of hexamethyldisiloxane.[4]

The polydimethylsiloxane structure has certain radiation chemical features which are quite different from other crosslinking-type polymers, such as polyethylene $(-CH_2CH_2-)_n$. Thus, the irradiation of dimethylsilicones causes both $\equiv Si-CH_3$ and $\equiv SiCH_2-H$ scissions with the evolution of H_2, CH_4, and C_2H_6 as the gaseous products. Recombinations of the two types of polymer radicals $\equiv Si\cdot$ and $\equiv SiCH_2\cdot$ can lead to three types of crosslinks. In linear polyethylene, the gaseous product is H_2 and only carbon–carbon crosslinks can be formed. Also, the polyethylene structure permits the formation of H_2 and *trans*-vinylene unsaturation without crosslinking,[5] while the dimethylsiloxane structure precludes the formation of unsaturation and consequently an exact correspondence between gas and cross-linking yields should be expected.

In the first paper of this series, measurements of crosslinking and evolved gas will be described for a polydimethylsiloxane oil in the glass state at liquid nitrogen temperature and in the fluid state between −40° and +150°. The effects of additives are reported in the second paper. On the basis of these

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(1) Presented, in part, at a Symposium on Chemical Effects of High Energy Radiation, A. A. A. S. Meeting, Washington, D. C., Dec. 26–31, 1958.

(2) F. A. Bovey, "Effects of Ionizing Radiation on Natural and Synthetic High Polymers," Interscience Publishers, Inc., New York, N. Y., 1958, p. 178.

(3) S. W. Kantor, Abstracts, 140th A. C. S. Meeting, Atlantic City, September, 1956, Div. of Org. Chem., Paper No. 94.

(4) H. A. Dewhurst and L. E. St. Pierre, Abstracts, 136th A. C. S. Meeting, Atlantic City, September, 1959, Div. of Polymer Chem. Papers No. 51 and 52.

(5) A. A. Miller, E. J. Lawton and J. S. Balwit, *J. Phys. Chem.*, **60**, 599 (1956); also E. J. Lawton, J. S. Balwit and R. S. Powell, *J. Polymer Sci.*, **32**, 257 (1958).

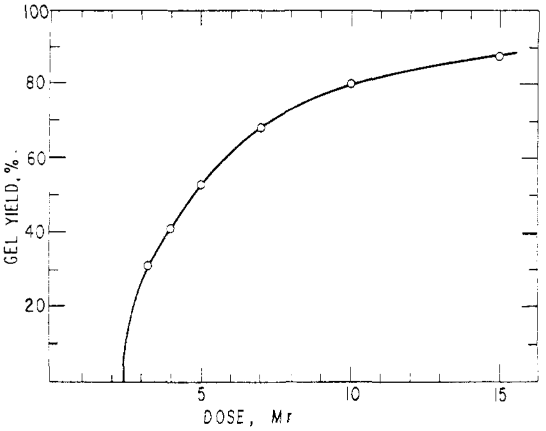

Fig. 1.—Gel yield as a function of irradiation dose for 30,000 c.s. polydimethylsiloxane oil ($\bar{M}_w$ = 85,000). Irradiated at 25° and an intensity of 13.8 Mr./min.

experimental measurements the kinetics and mechanism of the radiolysis of polydimethylsiloxane are discussed in the third paper of the series.

Experimental

A standard dimethylsilicone fluid (Viscasil 30,000) obtained from the G. E. Silicone Products Department was used. This material is a highly viscous oil with a bulk viscosity of 30,000 centistokes at 25°. The intrinsic viscosity measured in toluene at 25° was 35.5 cc./g., giving $\bar{M}_v$ = 76,000 on the basis of the relation $[\eta] = 0.0136\ M^{0.70}$.[6] Light-scattering measurements gave $\bar{M}_w$ = 85,000 (± 10%). Irradiations were done with 800 Kvp. electrons from a G. E. resonant-transformer unit on 2 gram samples in standard 2-inch aluminum dishes. The sample thickness was never more than 1 mm., the range of essentially uniform ionization for this type of radiation. Dosimetry was established in roentgen units with an air-ionization chamber; the calculation of radiation yields (G values) is based on an energy absorption of 5.2×10^{13} e.v./g./r. Unless otherwise specified, all irradiations were done at about 25° at a normal dose rate of 13.8 Mr./minute (1 Mr. = 10^6 r.) under a nitrogen atmosphere.

Following irradiation, the crosslinked gel was extracted by two 100 ml. portions of benzene, each for 24 hr. at room temperature. The extracted gel was dried to a constant weight by vacuum-pumping for 24 hr. Tests by additional extractions, which gave no further weight loss, showed that the adopted procedures gave complete extraction of the gel.

Differential, infrared spectroscopy was used to estimate certain specific groups formed by irradiation. In these cases, lower molecular weight polydimethylsiloxanes were used so that higher doses could be given before gelation. The absorption bands and absorption coefficients were determined by S. W. Kantor of this Laboratory from small model compounds especially synthesized for this purpose.[7] The values used were

Group	Infrared peak, μ	Absorp. coeff. (cm.²/mole) × 10⁻⁶
$\equiv$SiOH	2.72	1.1
$\equiv$SiH	4.63	1.4
$\equiv SiCH_2CH_2Si\equiv$	8.80	1.5
$\equiv SiCH_2Si\equiv$	7.38	0.17

The differential spectra were measured in a high-resolution Beckman Infrared-7 spectrometer using solutions in CS_2 or CCl_4, balanced against solutions of unirradiated polymer at the same concentration.

The $>$Si–Si$<$ group, which has no detectable infrared absorption, was measured by a bromination method also developed by Kantor.[7] This is a titrimetric procedure involving the rapid, quantitative reaction of bromine in carbon tetrachloride with the disilyl bond: $Br_2 + {>}Si{-}Si{<} \rightarrow 2SiBr$. Since the $\equiv$SiH bond also reacts rapidly, $>SiH + Br_2 \rightarrow {>}SiBr + HBr$, the total bromine absorbed must be corrected for the $>$SiH content, as measured by infrared analysis. For this determination, 2-gram samples of a 100 c.s.-silicone fluid were irradiated at 50 Mr. and the products swollen overnight in 50 ml. of CCl_4. Ten ml. of 0.1 N Br_2–CCl_4 solution was added and the sample stored in the dark for 15 and 30 minutes with frequent shaking. The unreacted Br_2 was determined iodometrically by addition of excess KI, following dilution with water, and titration with 0.1 N sodium thiosulfate. Blanks on 2-gram samples of unirradiated oil showed no reaction of the bromine in the 15 and 30 minute periods.

Gas yields were measured in a steel cell equipped with a mercury manometer and a thin (1 mil) stainless-steel window which was sealed by a flange and a lead O-ring. The 2-gram (1 mm. thick) sample of 30,000 c.s. silicone oil in the cell was thoroughly outgassed up to 100° on a high-vacuum line. Following irradiation, the cell was again heated to 100° to expel dissolved gases from the sample. For a 2-gram sample and a 10 Mr. dose, the typical pressures, measured at 25°, were 40 to 50 mm. Gas samples were analyzed on an analytical mass-spectrometer for which sensitivity calibrations for H_2, CH_4 and C_2H_6 were made periodically with the pure gases. The dosimetry was again determined by an ionization chamber in a "mock up" of the irradiation cell. This was confirmed by gel yields of the polymer samples following the gas measurements.

Results

Gel Measurements and Crosslinking Yields.—The gel yields for degassed samples of 30,000 c.s. silicone oil as a function of irradiation dose are shown in Fig. 1. Benzene solutions of the irradiated samples showed no gel at 2.0 and a trace of gel at 2.5 Mr. and this was considered as the dose required for incipient gelation. This was verified by a log sol *vs.* log dose plot which was linear and which extrapolated to 2.5 Mr. at 100% sol. In another series of measurements on samples containing dissolved air, a slight inhibition of gel formation was observed only at the lowest dose. Above 5 Mr. the gel yields were the same in the presence or absence of dissolved air. A more systematic study of the effect of oxygen will be presented in the next paper, but for the present it may be concluded that at doses of 5 Mr. and above the dissolved atmospheric oxygen is quickly consumed and there is no subsequent effect on the crosslinking.

On the basis of the criterion that incipient gelation occurs when there is one crosslink per two initial weight-average molecules[8] and the light-scattering measurement of $\bar{M}_w$ = 85,000 (±10%), we obtain G (crosslinks) = 2.7 ± 0.3 at 25° and an intensity of 13.8 Mr./min. Considering the 10% possible error in the initial light-scattering molecular weight determination and considering the gas yield (see below), a preferred value of G (c.l.) = 3.0 will be used.

The effect of irradiation temperature on the crosslinking yield was examined. Samples irradiated at temperatures up to 200° showed no significant weight loss, but at 300° a 10% loss due to volatilization occurred. The low temperature samples (−180 and −80°), which were in a glass state during irradiation, were restored to the fluid state at room temperature before exposure to air following irradiation. Gel yields were converted to "equiva-

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(6) F. P. Price, S. G. Martin and J. P. Bianchi, *J. Polymer. Sci.*, **22**, 49 (1956).

(7) S. W. Kantor, private communication. See A. M. Bueche, *ibid.*, **19**, 297 (1956).

(8) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 359.

lent doses" *via* the standard "calibration" curve (Fig. 1) and the relative crosslinking yield was calculated as the ratio of this "equivalent dose" to the delivered dose. The G values in Table I are the relative crosslinking yields normalized to a value of $G = 3$ at 25°.

TABLE I

EFFECT OF TEMPERATURE ON THE CROSSLINKING YIELD

Temp., °C.	G (crosslinks)
-180^a	1.9
-80^a	2.2
25	3.0
100	4.2
150	4.2
200	4.0
300	3.2

^{a} These were in the glass-state.

The crosslinking yield at 25° shows a small but definite intensity effect. Duplicate samples irradiated at 5 Mr. and at a dose rate of only 0.138 Mr./min. (a hundred-fold decrease from the normal dose rate), gave gel yields of 57%, corresponding to an "equivalent dose" (Fig. 1) of 5.5 Mr., or a 10% increase in crosslinking yield. Further gel measurements made in connection with the gas determinations (see below) also showed this intensity effect.

The yield of $\equiv$SiH groups was measured for irradiations at -180 (glass), 25 and 150° by infrared analysis. In these experiments, a lower molecular weight (100 c.s.) dimethylsilicone oil was used so that a sufficient dose could be given to produce a measurable change before gelation. For this oil, incipient gelation occurred at about 20 Mr., which corresponds to $\bar{M}_w \simeq 10{,}000$. Differential absorbance measurements at 4.63 μ were made on this undiluted oil in 1 mm. cells.

The infrared measurements for $>\mathrm{SiCH_2Si}<$ and $>\mathrm{SiCH_2CH_2Si}<$ were complicated by existing strong absorption bands in the 7 and 8 μ regions for the silicone polymer. Consequently, high irradiation doses on an even lower molecular weight silicone oil were required. By proper choices of dilution in CS_2 and cell thickness, detectable differential absorbances for the $>\mathrm{SiCH_2Si}<$ and $>\mathrm{SiCH_2CH_2Si}<$ could be obtained. Although the *trends* in these absorbances with irradiation temperature are fairly reliable, it should be emphasized that the absolute concentrations and, therefore, the radiation yields may be subject to considerable error. A 20 c.s. silicone oil with an incipient gel point at about 100 Mr. ($\bar{M}_w \simeq 2000$) was used here.

The data for the infrared measurements of $>\mathrm{SiH}$, $>\mathrm{SiCH_2Si}<$, $>\mathrm{SiCH_2CH_2}<$ and for $>\mathrm{Si{-}Si}<$ bonds by the bromination method, are listed in Tables II–IV.

Table V summarizes the radiation yields for the three types of crosslinks as a function of temperature. For the reasons given earlier, the data for $>\mathrm{SiCH_2Si}<$ and $>\mathrm{SiCH_2CH_2Si}<$ are reliable only to the extent of establishing trends with temperatures and not for absolute values of radiation yields. The errors are apparent in the comparison of the sum of the individual crosslinks, ΣG, with the total crosslink yields, as determined earlier from gel data.

TABLE II

DIFFERENTIAL INFRARED ABSORBANCES FOR $>$SiH. DOSE $=$ 10 MR.; 100% OIL IN 1.0 MM. CELLS

Temp., °C.	-180	$+25$	$+150$
$\Delta A_{4.63}$	0.044	0.052	0.086
(Mole $>$SiH/g.) $\times 10^6$	3.1	3.7	6.1
$G(>\mathrm{SiH})$	0.35	0.42	0.69

TABLE III

DIFFERENTIAL INFRARED ABSORBANCES FOR $>\mathrm{SiCH_2Si}<$ (7.38 μ) AND $>\mathrm{SiCH_2CH_2Si}<$ (8.8 μ) (DOSE $=$ 60 MR.)

Temp., °C.	-180	$+25$	$+150$
$\Delta A_{7.38\mu}$	0.0075^a	0.008^a	0.009^a
(mole/g.) $\times 10^4$	0.8	0.9	1.2
$G(>\mathrm{SiCH_2Si}<)$	1.5	1.8	2.3
$\Delta A_{8.8\mu}$	0.0038^b	0.0020^b	$\ldots^c$
(mole/g.) $\times 10^4$	5.1	2.7	...
$G(>\mathrm{SiCH_2CH_2Si}<)$	0.9	0.5	...

^{a} 10% solutions in CS_2; 0.49 mm. cells. ^{b} 1% solutions in CS_2; 0.49 mm. cells. ^{c} These measurements were not made.

TABLE IV

ANALYSIS FOR $>\mathrm{Si{-}Si}<$ BY BROMINATION (DOSE $=$ 50 MR.)

Temp., °C.	-180	$+25$	$+150$
Br_2 reacted (mole/g.) $\times 10^4$	0.07	0.69	0.97
$G(>\mathrm{Si{-}Si}< + >\mathrm{SiH})$	0.16	1.5	2.2
$G(>\mathrm{Si{-}Si}<)^a$	0	1.1	1.5

^{a} Using $G(>\mathrm{SiH})$ from Table II.

TABLE V

SUMMARY OF CROSSLINK YIELDS

Temp., °C.	-180	25	150
$G(>\mathrm{SiCH_2Si}<)$	(1.5)	(1.8)	(2.3)
$G(>\mathrm{SiCH_2CH_2Si}<)$	(0.9)	(0.5)	....
$G(>\mathrm{Si{-}Si}<)$	0	1.1	1.5
ΣG	(2.4)	(3.4)	....
$G(\text{crosslinks})^a$	1.9	3.0	4.2

^{a} From gel yields (Table I).

Gas Yields.—Hydrogen, methane and ethane constitute the gases evolved in the irradiation of polydimethylsiloxane. The yields of these gases as functions of irradiation temperature and intensity are shown in Table VI and the temperature effect is illustrated in Fig. 2.

TABLE VI

EFFECTS OF TEMPERATURE, RADIATION INTENSITY AND PHYSICAL STATE ON GAS YIELDS

	Temp., °C.	G(gas)	$G(H_2)$	$G(CH_4)$	$G(C_2H_4)$
13.8 Mr./min.	-180^a	2.8	0.95	1.62	0.22
	-40	2.7	1.19	0.71	.80
	25	3.1	1.25	1.07	.76
	100	3.9	1.37	1.96	.56
	150	5.1	1.45	3.0	.60
	200	6.0	1.24	4.17	.53
0.138 Mr./min.	-180^a	2.9	0.95	1.85	.10
	25	3.7	1.34	1.80	.54

^{a} Glass state.

Further gel measurements were made in the polymer irradiated in two of these gas determinations. At $-180°$ and a dose of 5 Mr. at 0.138 Mr./min. the total gas yield was 2.9 while the crosslinking yield was only 1.7. Also, at 200° and a dose of 5 Mr. at 13.8 Mr./min. the gas yield was 6.0 while the crosslinking yield was only 4.2.

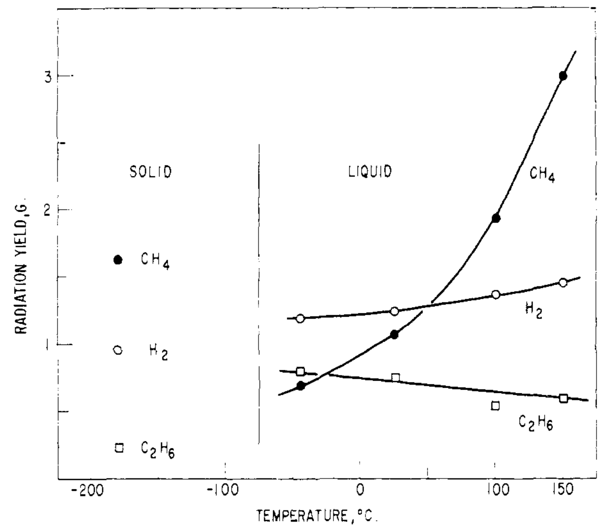

Fig. 2.—Gas yields for liquid and solid polydimethylsiloxane.

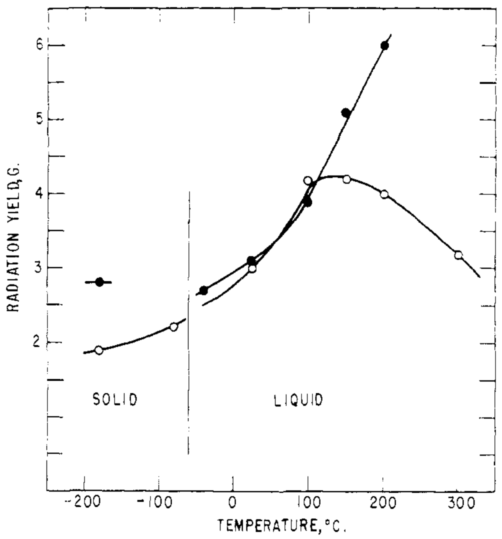

Fig. 3.—Comparison of gas yields (●) and crosslinking yields (○) for polydimethylsiloxane.

Discussion

In the liquid state between −40 and +100° good agreement between total gas yields and crosslinking yields is observed (Fig. 3). Indeed, such an equivalence is to be expected since the polydimethylsiloxane structure does not permit the formation of unsaturation. (Intramolecular cyclization, which could produce gas without intermolecular crosslinks, is assumed not to occur.) Above 100°, however, the two yields diverge markedly and a possible explanation is that an increasing amount of main-chain scission is occurring, causing a lower apparent crosslinking yield as measured by gel formation. If this were a simple free-radical cleavage, the equivalence between gas and crosslinking yields should still be maintained since the polymer fragments ($\geqslant$SiO· + ·Si$\leqslant$) could stabilize themselves only by (1) combination with the small H· and CH_3· radicals and this would decrease the gas yield correspondingly, or (2) hydrogen abstraction, which would produce equivalent amounts of new polymer radicals for crosslinking. Ordinary disproportionation of the polymer fragments is precluded in the siloxane structure. It is suggested that the decrease in apparent crosslinking yield at elevated temperatures is due to an ionic rearrangement of the siloxane backbone, possibly catalyzed by traces of ionic impurities[9] or by the radiation.

In the liquid state, at least up to 100°, both the crosslinking and gas yields show a positive temperature coefficient and also a small but definite increase with decreased radiation intensity. A reasonable explanation for these effects is a competition between recombinations of H· and CH_3· radicals and their hydrogen abstraction on polymer molecules to produce additional polymer radicals, with the abstraction reactions being favored by increased temperatures and/or decreased intensity.[10] These competing radical reactions also account for the observed changes in CH_4 and C_2H_6 yields with temperature and intensity. It should be noted that the H_2 yield is considerably less sensitive to both of these factors than is the CH_4 yield. It may be significant that in the radiolysis of liquid neopentane, $C(CH_3)_4$, where methyl groups are also involved, it was observed that the CH_4 yield increased with temperature while the H_2 yield remained essentially constant.[11] In the cited work, however, the effect of radiation intensity was not examined, nor was the yield of C_2H_6, if any, reported.

For the radiolysis at low temperature in the rigid glass state the following interesting features should be noted. Although considerable scission of CH_3 groups still occurs, as evidenced by the CH_4 and C_2H_6 yields, mutual recombination of the expected $\geqslant$Si· polymer radicals has been suppressed, since $\geqslant$Si–Si$\leqslant$ crosslinks are absent (Table IV). Recombination of $\geqslant$Si· and H· is still important, however, as shown by the $\geqslant$SiH yield. A surprising result is the large *increase* in CH_4 yield in the transition from the liquid to the glass-state. It seems unlikely that this change in CH_4 yield can be attributed to an increased hydrogen abstraction by thermal CH_3· radicals, occurring to a greater extent in the glass-state at −180° than in the fluid state at higher temperatures. A further anomalous effect in the glass-state is that the crosslinking yields were always significantly lower than the gas yields (Fig. 3). Although entrapment of the large polymer radicals may prevent their immediate crosslinking in the rigid glass matrix, these radicals should still combine to form crosslinks, corresponding to the gas evolved, when the sample is thawed to the fluid state in the absence of oxygen following irradiation.

A tentative explanation for these apparently anomalous radiation effects in the transition from the liquid to the glass-state is that one or more of the primary radiation chemical processes are significantly altered. Thus, to explain the difference be-

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[9] See C. W. Lewis, *J. Polymer Sci.*, **37**, 425 (1959).

[10] A. Charlesby, W. H. T. Davison and D. G. Lloyd, *J. Phys. Chem.*, **63**, 970 (1959), have reported a similar dependence of the crosslinking yield on intensity over a much wider intensity range. However, they attributed this to "track" and LET effects rather than competing radical reactions.

[11] M. Hamashima, R. P. Reddy and M. Burton, *ibid.*, **62**, 246 (1958).

tween the total gas and crosslinking yields and also the simultaneous increase in CH_4 yield in the glass-state at $-180°$, it is suggested that here an appreciable fraction ($G \simeq 0.9$) of the CH_4 is formed by a "molecular" primary process which involves neither $CH_3\cdot$ radicals nor polymer radicals as intermediates. Further discussion will be presented in a subsequent paper of this series.

Acknowledgment.—Miss D. McClung made the infrared measurements and P. C. Noble the mass spectrometer analyses. E. J. Lawton and J. S. Balwit assisted in the design of the gas measurement cell and provided the dosimetry. All irradiations were done by J. S. Balwit. In particular, the author is indebted to S. W. Kantor for providing unpublished infrared data on siloxanes.

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY, PRINCETON, NEW JERSEY]

Microwave Absorption and Molecular Structure in Liquids. XXX. The Anomalous Dielectric Relaxation of Diphenyl Ether and Some Similar Molecules[1,2]

BY D. M. ROBERTI,[3] O. F. KALMAN AND C. P. SMYTH

RECEIVED NOVEMBER 25, 1959

Dielectric relaxation times have been determined for diphenylmethane, benzyl ether, bibenzyl and dibenzyl ether, as pure liquids, to be compared with previous values for diphenyl ether and benzophenone. All the measured compounds have relaxation times comparable to that for diphenyl ether, very low in comparison to that for benzophenone. In addition, the relaxation time of diphenyl ether measured in Nujol has been found to be relatively insensitive to viscosity and temperature. The results indicate that some form of intramolecular motion is responsible for the small relaxation time. Several previously proposed mechanisms are discussed.

The relaxation time of diphenyl ether in benzene was found by Fischer[4] to be 0.28×10^{-11} sec., a value seemingly much too small when compared with the value of 2.04×10^{-11} sec. for benzophenone, a molecule of approximately the same size and shape. The anomalously low relaxation time of diphenyl ether has interested a number of investigators, and the findings of Fischer have been approximately confirmed by measurements using other methods.[5,6]

The present research is an attempt to elucidate the problem by measuring the relaxation times of some molecules similar to diphenyl ether. In addition, measurements have been made on diphenyl ether in dilute solutions in Nujol.

Purification of Materials.—Diphenyl ether, obtained from Matheson, Coleman and Bell, Inc., was dried with calcium chloride and fractionally distilled under reduced pressure. It was crystallized slowly at 25–27° and a small portion poured off. The final product had a refractive index $n^{30.65}\mathrm{D}$ 1.57596. Dibenzyl ether, obtained from Brothers Chemical Co. and distilled under reduced pressure, gave a density d^{20} 1.0424 and $n^{20}\mathrm{D}$ 1.56264. Benzyl phenyl ether was synthesized according to the procedure of Peacock,[7] dried over calcium, fractionally distilled under reduced pressure and recrystallized from heptane. The final product had $d^{40} = 1.0518$ and a melting point of 36°. Diphenylmethane, from Matheson, Coleman and Bell, Inc., was fractionally distilled twice under reduced pressure, finally boiling at 114.5° at 6 mm. pressure, giving a d^{30} of 0.9971. Bibenzyl, obtained from Matheson, Coleman and Bell, Inc., was fractionally distilled, boiling at 270–271°, with a melting point of 51.2°.

Experimental Results

Dielectric constants, ϵ', and losses, ϵ'', at wave lengths of 1.25 and 3.22 cm. and the so-called static dielectric constant, ϵ_0, were measured over a range of temperatures by methods described or referred to in earlier papers of this series.[8] In the case of dibenzyl ether, measurements also were made at 10.0 cm. wave length. For some substances, measurements could not be made at lower temperatures because of high melting points. Densities were determined with a graduated pycnometer and viscosities with an Ostwald-Fenske viscometer. The values obtained for the liquid measurements at each temperature are given in Table I. For the solution measurements, Table II gives values of the slopes of the square of the refractive index, a_D, static dielectric constant, a_0, dielectric constant, a', and loss, a'', against the weight fraction of solute in solutions in Nujol made up from a specimen designated as Nujol (II).

From the dielectric constant data Cole–Cole arc plots were drawn and used to determine the critical wave lengths, λ_m, at which the loss is a maximum. Table III contains the values of the optical dielectric constants, ϵ_∞, the distribution parameters, α, and the critical wave lengths obtained from the arc plots. From the critical wave length, the macroscopic relaxation time, τ_M, is calculated according to the equation $\tau_M = \lambda_m/2\pi c$. To correct for the effect of dipole–dipole interaction in the liquid state, the Powles[9] internal field correction, found to be the most nearly correct form in a recent evaluation,[10] gives a molecular relaxation time, τ_μ. Values of τ_μ and of the dipole moments, μ, calculated from ϵ_0 and ϵ_∞ values by the Onsager equation are also

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(2) This paper represents a part of the work submitted by D. M. Roberti to the Graduate School of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Portions of this paper were read before the American Chemical Society, Division of Physical Chemistry, Atlantic City, N. J., Sept. 16, 1959.

(3) Gulf Oil Fellow in Chemistry, 1957–1958.

(4) E. Fischer, *Z. Elektrochem.*, **53**, 16 (1949).

(5) F. Dieringer, *Z. Physik*, **145**, 184 (1956).

(6) J. H. Calderwood and C. P. Smyth, THIS JOURNAL, **78**, 1295 (1956).

(7) D. H. Peacock, *Proc. Chem. Soc.*, **30**, 247 (1914).

(8) R. S. Holland and C. P. Smyth, *J. Phys. Chem.*, **59**, 1088 (1955).

(9) J. G. Powles, *J. Chem. Phys.*, **21**, 633 (1953).

(10) R. C. Miller and C. P. Smyth, THIS JOURNAL, **79**, 3310 (1957).