

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

Chemical Stress-Relaxation of Polydimethylsiloxane Elastomers¹

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The study of the chemical stress-relaxation of polydimethylsiloxane elastomers has been used to elucidate the catalytic behavior of acids and bases toward siloxane rearrangement reactions. It has been shown that acids and bases both catalyze a siloxane rearrangement reaction which causes stress-relaxation to occur. It was also found that water and carbon dioxide contribute to the rate of stress-relaxation, *i.e.*, siloxane rearrangement, in the presence of acids or bases in the siloxane elastomer. The measurement of the rate of stress-relaxation on pure polydimethylsiloxane systems at various temperatures leads to an activation energy of 22.8 kcal. mole⁻¹ for the relaxation process. The apparent activation energy for stress-relaxation of a polydimethylsiloxane elastomer containing 0.01% of potassium hydroxide was found to be only 5.1 kcal. mole⁻¹ indicating the activity of the base in promoting siloxane rearrangements.

I. Introduction

The study of the chemical stress-relaxation of polymeric materials makes possible the investigation of the behavior of reagents in cases in which the actual extent of reaction is very small or in which the system after reaction is chemically similar to that before. With this in mind the authors have studied the stress-relaxation properties of various polydimethylsiloxanes. Thus, it was possible to study reactions occurring under various conditions in cases in which there was no visible change in the polysiloxane elastomer.

II. Experimental

The experiments were carried out in an electrically heated glass tube into which the test sample of polydimethylsiloxane elastomer was placed. A heater of nichrome ribbon was so constructed around the tube that the temperature within could be maintained to $\pm 1^\circ$ in the temperature range of 25 to 250°. The stress-relaxation apparatus was constructed in such a manner that various gases could be passed through the thermostat in order to conduct experiments in a controlled atmosphere. The cable which exerted tension on the samples was passed over ball bearing pulleys and finally connected to a pan. By placing weights on the pan the tension on a sample could be determined to ± 1 gram. The test samples were elongated to any desired extent, by adjusting the pan stop to the position corresponding to the required elongation. Thus in operation the sample in the clamps was elongated to the desired degree and the stress required to maintain this elongation was measured at various times. One obtained, in this manner, a stress-relaxation curve at constant temperature and elongation.

Gums.—The gums employed in this study were prepared according to the method of Hyde.² Five hundred grams of octamethylcyclotetrasiloxane was polymerized with 0.01% of potassium hydroxide by heating at 150° for 1 hour. The resulting gum was milled with 1.65 wt. % of benzoyl peroxide³ and the material was then press cured in thin sheets (1.7 to 1.9 mm. in thickness) for 20 minutes at 125° followed by an additional 16 hour oven cure in an air oven at 150°. Dumbbell shaped samples were cut from the sheets and the samples were stored in a desiccator over anhydrous calcium sulfate until used. It is to be observed that these samples contained 0.01% of potassium hydroxide and no attempt was made to remove this material from this initial group of cured sheets. However, in some experiments it was desired to employ catalyst-free gum, *i.e.*, gum from which the residual potassium hydroxide polymerization catalyst had been removed. This was accomplished by dissolving the polydimethylsiloxane which had not been cross-linked in anhydrous toluene. This solution was then shaken thoroughly with a dilute aqueous solution of hydrogen chloride of such a concentration that there was a slight stoichiometric excess of acid over the 0.01% of potassium hydroxide which was in the gum. The toluene solution was then

separated and repeatedly washed with distilled water until the washings showed no test for the presence of chloride ion. At this point the polymer solution was dried over anhydrous sodium carbonate and then added to excess anhydrous methanol in order to precipitate the polydimethylsiloxane. The precipitated gum was washed five times with anhydrous methanol and finally freed of solvent by pumping on a high vacuum system, until the pressure above the gum was reduced to 50 μ of mercury at room temperature.

Studies with Gum Containing Residual Potassium Hydroxide.—Initially the stress-relaxation of the gum containing 0.01% of potassium hydroxide was studied at 25° in an atmosphere of air and in an atmosphere of dry nitrogen (samples at 80% elongation). The typical stress-relaxation curves of Fig. 1 were obtained in this fashion. In this and subsequent figures the logarithm of the stress is plotted against time. The difference in the rate of stress-relaxation in air and in dry nitrogen was very small at 25°, but the effect was greatly accentuated when the experiments were carried out at 130°. These results are also illustrated in Fig. 1. It will be seen that the rate of stress-relaxation in

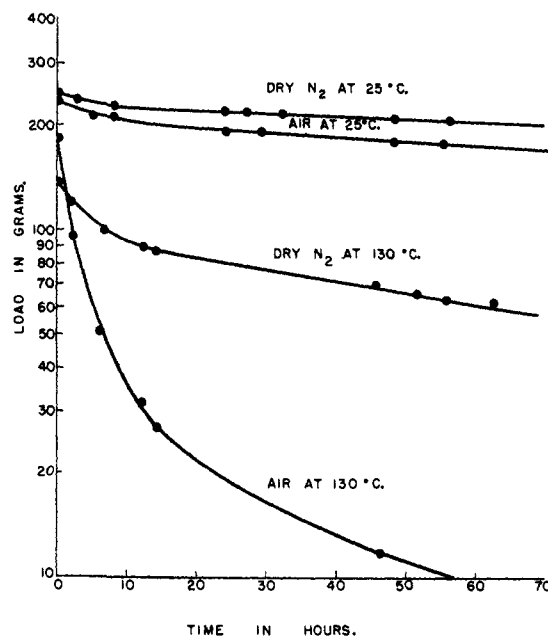


Fig. 1.—Stress-relaxation of polydimethylsiloxane gum containing 0.01% potassium hydroxide and benzoyl peroxide fragments in air and nitrogen at 25 and 130°.

air is much more rapid than in dry nitrogen under the conditions of the experiment. It was thus concluded that oxygen, water vapor or carbon dioxide of the air were active in contributing to the stress-relaxation of the siloxane polymer from which the 0.01% of potassium hydroxide had not been removed. That water is particularly effective in causing stress-relaxation is indicated in Fig. 2, in the case of the experiment from which the data from Fig. 2 were obtained,

(1) Presented before the Division of Polymer Chemistry, 125th American Chemical Society Meeting, Kansas City, Mo., March, 1954.

(2) James Franklin Hyde, U. S. Patent 2,490,357 (April 24, 1946).

(3) W. B. Spencer, Jr., W. B. Davis and F. L. Kilbourne, Jr., *Ind. Eng. Chem.*, **45**, 1297 (1953).

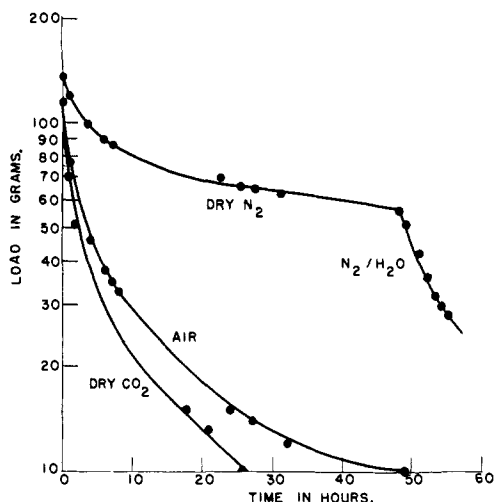
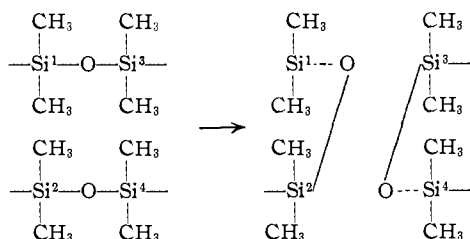


Fig. 2.—Effect of water, air and carbon dioxide on stress-relaxation rates at 130° (gum containing 0.01% potassium hydroxide and peroxide fragments).

the stress-relaxation run was commenced in an atmosphere of dry nitrogen at 130°. After 50 hours the nitrogen passing into the stress-relaxation apparatus was saturated with water at room temperature before entering the sample zone. It will be seen that the rate of stress-relaxation was greatly accelerated in the presence of the water. Also shown in Fig. 2 are stress-relaxation curves made in the presence of air and of anhydrous carbon dioxide. It is clear that carbon dioxide also causes a rapid stress-relaxation to occur. In a separate experiment it was shown that oxygen has no effect on the rate of stress-relaxation at 130° since the same rate was obtained in the presence of oxygen as was obtained in the case in which the atmosphere was dry nitrogen. This stress-relaxation process may be attributed to some sort of chain rupture which tends to relieve stress within the polymer. A typical reaction which would serve as a possible basis for theoretical interpretation of this process is the so-called chain exchange reaction.⁴



(In this case, the numbers appearing as superscripts to the silicon atoms are merely used to differentiate the various atoms involved in the reaction.)

The results of the present study eliminate the possibility of stress being relieved by mechanisms other than chain exchange, *i.e.*, chain rupture with subsequent termination. This is strikingly shown by the experiments represented in Fig. 3. These data indicate conclusively that the chains responsible for the initial tension are reformed in a relaxed state during the stress-relaxation process, since on the second stretch tension is encountered and a similar relaxation process again occurs. It has been shown⁶ that the shape of the stress-relaxation curve is indicative of the mechanism of the relaxation process. The shapes of the curves presented here are not inconsistent with the chain exchange mechanism. It is conceivable, however, that other reagents might cause chain rupture followed by termination. This is presumably the case when the rate of stress-relaxation is increased by the presence of water vapor (*cf.* Fig. 2). Presumably the rapid decay of stress in the presence of water

(4) This mechanism was first proposed by D. T. Hurd, private communication, April, 1952.

(5) A. M. Bueche, *J. Chem. Phys.*, **21**, 614 (1953).

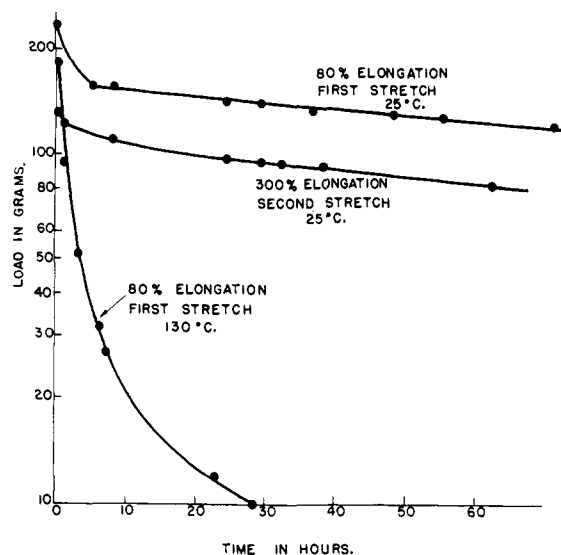


Fig. 3.—Repeated stress-relaxation on a single sample at 25° (gum containing 0.01 KOH and peroxide fragments). Run at 130° presented for comparison.

involves the scission of the siloxane bond with the subsequent formation of silanols: $-\text{SiOSi}- + \text{H}_2\text{O} \rightarrow 2-\text{SiOH}$.

Once the stress has been partially relieved by such a chain rupture, the silanol groups are free to condense again in the relaxed state.⁶ The above equation then constitutes a possible mechanism for a chain exchange reaction in the presence of water.

In a series of separate experiments with the potassium hydroxide gum, it was shown that the rate of stress-relaxation was independent of elongation in the range of 65–100%.

Experiments with Catalyst-free Gum.—A batch of catalyst-free polydimethylsiloxane elastomer was cross-linked with 1.65% of benzoyl peroxide by treatment as described above. Samples of this material were stretched and allowed to relax in the presence of dry nitrogen and nitrogen plus water. The results of these experiments are represented graphically in Fig. 4. It is to be observed that a relaxation process still occurs and that the relaxation of stress is accelerated when water is present. It is assumed in this case that the mechanism for stress relaxation is of the same nature, *i.e.*, chain exchange reactions, as in the case of the polymer which still contained the basic catalyst. However, in this case the catalyst was assumed to be the acidic fragments formed by the decomposition of benzoyl peroxide in

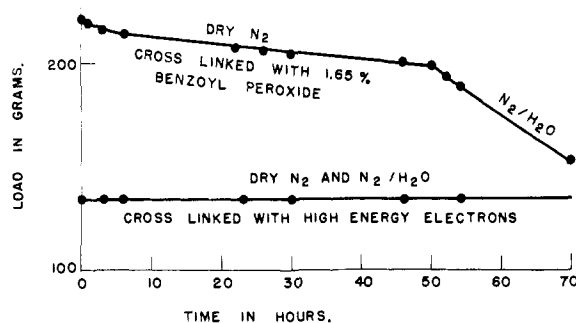


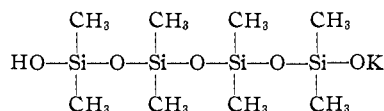
Fig. 4.—Stress-relaxation of catalyst-free polydimethylsiloxanes cross-linked with benzoyl peroxide and with high energy electrons.

(6) W. T. Grubb, "A Study of Silanol Condensations," paper presented before the Division of Physical and Inorganic Chemistry, 124th American Chemical Society Meeting, Chicago, Illinois, September 6, 1953.

the siloxane.⁷ In order to obtain a polydimethylsiloxane elastomer which had been cross-linked, but which was free of acidic residues as well as basic materials, a sample of catalyst-free gum was subjected to irradiation with high energy electrons (dosage of 10^7 R with 800 kev. electrons).⁸ An examination of Fig. 4 clearly indicates that no stress-relaxation occurred with this gum in which no acidic or basic residues were present. In fact, no relaxation of stress was observed even in the presence of carbon dioxide or water vapor at 130° .

In Situ Neutralization of Basic Catalyst.—Since the above data clearly indicate the catalytic role of acids and bases in promoting stress-relaxation in polydimethylsiloxane systems, an attempt was made to neutralize the residual potassium hydroxide *in situ*. Previous work⁹ had shown that iodine diffused rapidly in polysiloxanes so its reaction with potassium hydroxide was investigated.

In a series of open tube experiments samples of octamethylcyclotetrasiloxane containing 0.01% of potassium hydroxide in suspension were heated to 150° . In a typical experiment the potassium hydroxide particles dissolved (or reacted) within 3 to 5 minutes and a high polymer was formed in approximately 1 hour. A viscosity of 750,000 centipoise as determined by means of a Brookfield viscometer at 150° was obtained after a 1 hour polymerization time. The effect of adding a crystal of iodine (about 0.05 g.) to a duplicate system was to halt the polymerization completely. No polymerization took place in 24 hours at 150° . The excess of iodine escaped by evaporation and a white to brownish precipitate remained behind. The same results were obtained whether the iodine was added immediately to the 0.01% potassium hydroxide suspension in octamethylcyclotetrasiloxane, or after the potassium hydroxide had dissolved at 150° . This observation is of particular interest in view of the hypothesis¹⁰ that such structures as:



are formed when potassium hydroxide dissolves in octamethylcyclotetrasiloxane at elevated temperature. Since it is difficult to conceive of a reasonable mechanism for the neutralization of iodine by either $-\text{Si}-\text{OH}$ or $-\text{Si}-\text{OK}$ in a siloxane medium, it is proposed that $-\text{Si}-\text{OK}$, if present, exists either in equilibrium with potassium hydroxide in solution or as a transient intermediate in siloxane rearrangement and polymerization reactions. These experiments indicated that iodine destroyed the potassium hydroxide polymerization catalyst and suggested the use of iodine to produce a decatalyzed gum for measurements of the stress-relaxation. Samples of polydimethylsiloxane gum which contained 0.01% of potassium hydroxide were treated with 0.06% of iodine. These samples were then heated to 250° in an air oven for 1 hour to remove the excess iodine. The samples were then irradiated at a dose level of 10^7 R with 800 kev. electrons as described previously. Several samples of the gums prepared in this way were then subjected to the measurement of stress-relaxation. In Fig. 5 is illustrated a typical stress-relaxation curve for the iodine treated sample as well as for a decatalyzed sample of polydimethylsiloxane gum. It may be seen that the iodine produces a material which gives a rate of stress-relaxation which is comparable to that of the decatalyzed gum. It was thus of interest to investigate the nature of the iodine-potassium hydroxide reaction in more detail.

To 182 g. of octamethylcyclotetrasiloxane containing 0.01% of potassium hydroxide was added 0.06 wt. % of iodine and the solution was then heated at 150° for 20 minutes. The mixture was suction filtered and a small amount of precipitate was recovered which was washed several times with benzene. There was recovered from the

(7) S. W. Kantor and R. C. Osthoff, unpublished data, 1952. It has been shown that acidic residues are formed by the decomposition of benzoyl peroxide at 120° in a siloxane medium, benzoic acid and *p*-phenylbenzoic acid constituting the major portion of the acidic residues.

(8) E. J. Lawton, A. M. Bueche and J. S. Baldwin, *Nature*, **172**, 76 (1953).

(9) W. T. Grubb, unpublished data, 1952.

(10) D. T. Hurd, R. C. Osthoff and M. L. Cortin, *THIS JOURNAL*, **76**, 249 (1954).

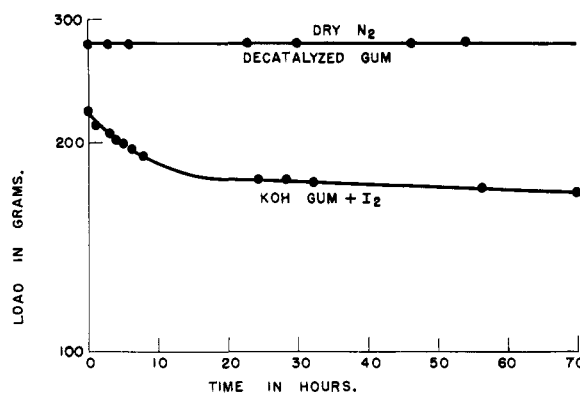
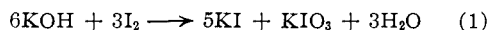


Fig. 5.—Stress-relaxation of catalyst-free polydimethylsiloxane and of iodine-treated potassium hydroxide gum.

filter 0.088 g. of a brownish precipitate. A powder X-ray photo of the above product was identical with that obtained from a 5:1 molar mixture of potassium iodide plus potassium iodate. This offers strong evidence that only potassium iodide and potassium iodate are present in major amounts in the reaction products of potassium hydroxide with iodine at 150° in octamethylcyclotetrasiloxane. Probably then, the reaction is



A conventional wet analysis of the product obtained from the reaction of iodine with potassium hydroxide in octamethylcyclotetrasiloxane gave a potassium iodide to potassium iodate ratio of 5.94 with an analytical error estimated to be about 1%. In view of the strong oxidizing power of potassium iodate, some reaction with octamethylcyclotetrasiloxane at 150° or some thermal decomposition may well account for the difference between 5.94 and the value 5.00 required by equation 1 above.

Activation Energy of Stress-Relaxation.—It has been shown⁴ that for a chain scission process of first order, occurring at random in a randomly cross-linked sample, the tension τ is related to the time, t , by

$$\tau = 2RT(X_0 - N_0)\rho[\exp.(Kt) - 1 + \rho]^{-1}\phi(\alpha) \quad (2)$$

where

R is the gas constant

T is the absolute temp.

X_0 is the no. of moles of cross-links/unit volume of polymer

N_0 is the no. of moles of polymer/unit volume before cross-linking

ρ is the reciprocal of the degree of polymerization of polymer chains between cross-links

K is proportional to the rate constant for the chain scission process

$\phi(\alpha)$ is a function of the elongation α of the sample and defines the shape of the stress elongation curve

Equation 2 may be expanded to give equation 3

$$\frac{1}{\tau} = A \left[1 + \frac{Kt}{\rho} + \frac{(Kt)^2}{\rho^2!} + \frac{(Kt)^3}{\rho^3!} + \dots \right] \quad (3)$$

where

$$A = [2RT(X_0 - N_0)\phi(\alpha)]^{-1}$$

As indicated by equation 3, K may be evaluated at various temperatures by plotting $1/\tau$ vs. the time, t . The activation energy is then obtained from the conventional plot of the logarithm of the rate constant against the reciprocal of the absolute temperature.

It would seem to be of interest to examine rate of stress-relaxation for polydimethylsiloxane elastomer containing 0.01% of potassium hydroxide and for the catalyst free elastomer in an attempt to ob-

tain activation energies for the chain exchange reaction. Samples of the polydimethylsiloxane gum which contains 0.01% of potassium hydroxide, and which were cross-linked with 1.65% of benzoyl peroxide, were subjected to measurements of stress-relaxation at 60, 100 and 140°. These data are illustrated in the graph of Fig. 6. The recipro-

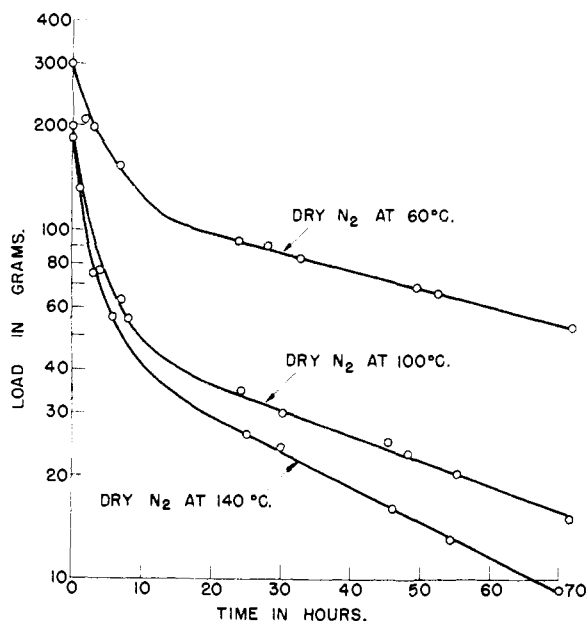


Fig. 6.—Stress-relaxation of polydimethylsiloxane (containing 0.01% KOH) at various temperatures.

vals of the tension were fitted with a quadratic expression in time. The first term in the quadratic divided by the intercept at $t = 0$ was assumed to be proportional to the rate constant in accordance with equation 3. In this fashion values of K/ρ could be obtained. Little significance could be attached to the coefficient of the term in t^2 . Thus, the values of K/ρ were then plotted on a logarithmic scale as a function of the reciprocal of the absolute temperature. The observed data are presented in Table I. The apparent activation energy was obtained in the usual fashion and was found to be 5.1 kcal. mole⁻¹. The relatively low value of 5.1 kcal. mole⁻¹ for the apparent activation energy stress-relaxation of the polydimethylsiloxane containing 0.01% of potassium hydroxide and the acidic residues from the decomposition of benzoyl peroxide is not surprising in view of the relative ease with which dimethylsiloxanes undergo chain exchange reactions in the presence of acidic or basic catalysts.

TABLE I
APPARENT ACTIVATION ENERGY OF STRESS-RELAXATION OF
POLYDIMETHYLSILOXANE CONTAINING 0.01% POTASSIUM
HYDROXIDE

$t, ^\circ\text{C.}$	$10^3/T$	$\ln [K/\rho \times 10^3]$
60	3.00	3.25
100	2.68	4.12
140	2.42	4.77

A similar series of experiments in the temperature range of 150 to 260° were carried out with catalyst free gum which was cross-linked with high en-

ergy electrons. These measurements were conducted in an atmosphere of anhydrous argon in order to eliminate any effect of oxidation reactions which might occur at these elevated temperatures. The data obtained in this fashion are represented in the stress-relaxation curves of Fig. 7 in which runs at 150, 180, 200, 235 and 260° are represented.

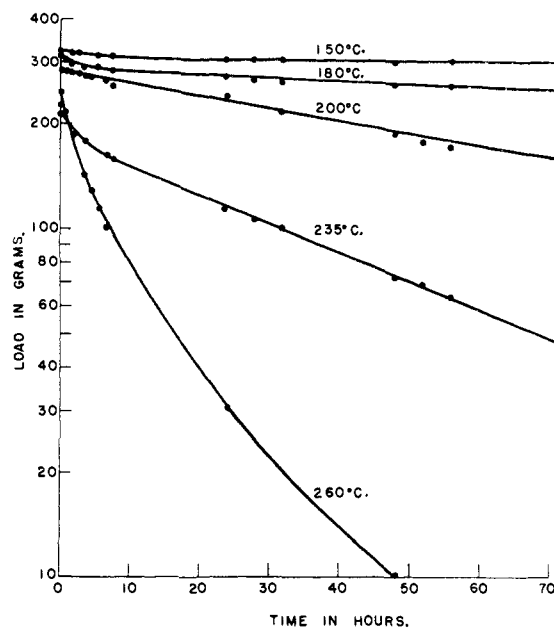


Fig. 7.—Stress-relaxation curves for catalyst-free polydimethylsiloxanes at various temperatures.

Again in this case the activation energy for stress-relaxation was evaluated by plotting reciprocal tension *vs.* time and determining the values of K/ρ as before. The data for these experiments are presented in Table II.

TABLE II
ACTIVATION ENERGY OF STRESS-RELAXATION OF CATALYST-FREE
POLYDIMETHYLSILOXANE ELASTOMER IN ANHYDROUS
ARGON

$t, ^\circ\text{C.}$	$10^3/T$	$\ln K/\rho \times 10^3$
150	2.36	0.051
180	2.21	1.11
200	2.12	2.43
235	1.97	4.01
260	1.87	5.28

The value of the activation energy found in this fashion was 22.8 kcal. mole⁻¹. The difference in activation energies between this value and the value for the polymer which contained potassium hydroxide and benzoyl peroxide decomposition fragments is indicative of the sensitivity of siloxanes to these materials. The value of the activation energy of stress-relaxation for decatalyzed polydimethylsiloxane elastomers in anhydrous argon of 22.8 kcal. mole⁻¹, represents a value in the range expected for chemical reactions. Presumably this is the activation energy of the chain exchange reaction. The chain exchange mechanism is believed to constitute the primary process involved in the stress-relaxation of siloxanes, and it has been

clearly shown that this reaction is catalyzed by acids and bases, and thus one would expect lower activation energies (and higher rates for stress-relaxations) of samples contaminated with trace amounts of catalytically active materials.

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SCHENECTADY, N. Y.

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The Crystal Structure of Isonicotinic Acid Hydrazide¹

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The crystal structure of isonicotinic acid hydrazide has been solved by two-dimensional projections. Within the pyridine ring, the C-C bonds are all within experimental error of the expected values while the C-N bond lengths are somewhat less than the usually accepted value. The N-N bond length is within experimental error of the covalent radii sum (1.40 Å.) but considerably less than the value for hydrazine (1.46 Å.).

Isonicotinic acid hydrazide is the monosubstituted hydrazide of pyridine-4-carboxylic acid. This investigation was carried out to provide relatively accurate molecular parameters, bond lengths and angles, from the solid state structure of this biologically important compound.

Unit Cell and Space Group.—Crystals of isonicotinic acid hydrazide satisfactory for X-ray diffraction studies were supplied by E. K. Squibb & Co. Crystals of the same phase and habit grow from 95% ethanol as well developed needles elongated in the direction of the *c*-axis with {010} and {120} prominent.

The unit cell and space group were determined from equi-inclination Weissenberg and rotation photographs about the *a*- and *c*-axes using Cu K_α radiation ($\lambda = 1.542$ Å.). The dimensions of the orthorhombic unit cell were found to be: $a_0 = 11.33$ Å.; $b_0 = 14.74$ Å.; $c_0 = 3.84$ Å., with an error estimated as $\pm 0.3\%$.

The density measured by flotation was found to be 1.411 g.cm.⁻³; calculated, 1.420 g.cm.⁻³ assuming 4 molecules in the unit cell. All (*h*00), (0*k*0) and (00*l*) reflections for odd *h*, *k* and *l*, respectively, were absent. Since no other systematic absences were found, the space group was assumed to be P2₁2₁2₁ with four asymmetric molecules lying in general positions.

Intensity Data.—Data were collected using a number of crystals of different size. The smaller crystals were used to minimize extinction effects, the larger to maximize the number of observed reflections. Crystals used for (*hk*0) were of fairly uniform cross-section, but for the other two axial zones it was necessary to cut the crystals to reduce absorption effects.

Some difficulty was experienced in obtaining consistent intensities for the most intense reflections from different crystals. Presumably the effect was due to extinction since it was dependent on the size and history of the crystal. One crystal was immersed repeatedly in liquid nitrogen; this reduced but did not eliminate the effect.

Several exposures using multiple films were taken for each of the three axial zones. The camera used

was an integrating Weissenberg type² set to integrate along the film coordinate at right angles to the rotation axis. The optical density was measured on a Moll type microphotometer³ feeding into a speedomax recorder by scanning along the film coordinate at right angles to the direction of integration by the camera. The integrated intensity was taken as proportional to the area under the curve of optical density *vs.* film coordinate within the linear response limits of the film used. For some of the weakest reflections, data were taken from unintegrated photographs, peak heights of the photometric tracings being assumed proportional to intensities. Of the 322 principal zone reflections accessible, 51 were too weak to observe even on prolonged exposure.

Intensities from the films for each axial zone were brought to an arbitrary scale by multiplying by appropriate scale factors, dividing by the Lorentz and polarization factors, and converted to relative values, $|F_r|$. Finally data for each zone were brought onto an absolute scale by multiplying by $\Sigma|F_c|/\Sigma|F_r|$.

In an earlier communication it was reported that Wilson's method of putting the *hk*0 intensities on an absolute scale yielded values which were too high.⁴ That result was partly due to a pair of errors. A plot of the eye estimated data for $\sin \theta < 0.75$ indicates a negligible temperature factor and a scale factor high by *ca.* 1.7 instead of *ca.* 3 as reported. However, a similar plot using integrated intensities for the *complete* range accessible to Cu K_α radiation results in a temperature factor of expected magnitude and a scale factor within 10% of the final value. Calculation of the root-mean-square unitary structure factors including the temperature factor and consideration of the number of unobserved reflections for the eye estimated data accounts satisfactorily for the difficulties noted in the early data.

Scattering factors as listed by McWeeny⁵ were used in calculating structure factors, F_c . An isotropic temperature factor, $e^{-B \sin^2 \theta / \lambda^2}$ was assumed for F_{hk0} and an anisotropic factor, $e^{-(B + C \cos^2 \phi) \sin^2 \theta / \lambda^2}$

(2) E. H. Wiebenga and D. N. Smits, *Acta Cryst.*, **3**, 265 (1950).

(3) H. S. Bennett, *et al.*, *Applied Spectroscopy*, **7**, No. 3 (1953).

(4) L. H. Jensen, *Nature*, **171**, 217 (1953).

(5) R. McWeeny, *Acta Cryst.*, **4**, 513 (1951).

(6) L. Helmholtz, *J. Chem. Phys.*, **4**, 316 (1936).

(1) Presented at the 124th meeting of the American Chemical Society, Sept., 1953.