

Creep under Constant Load in Tension

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Letters to the Editor

THIS section will accept reports of new work provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge (\$3.00 per page) will not be made and no reprints will be furnished free.

Latin American Collaboration

HARLOW SHAPLEY

Chairman of the Committee on Inter-American Scientific Publication,
Harvard College Observatory, Cambridge, Massachusetts
November 8, 1945

SCIENTISTS in the United States are cooperating with their colleagues in Latin American countries by contributing files of scientific journals to a number of new and active institutions in these countries where lack of such facilities is greatly impeding research. This work is being carried on by the Committee on Inter-American Scientific Publication, headed by Harlow Shapley, and already the libraries of two such institutions have been assisted in this way.

The committee is now collecting journals for a number of other institutions in Latin America and is particularly eager to receive contributions of unused files of chemical periodicals for this purpose. We hope that any persons who wish to assist in this very genuine and timely method of promoting hemispherical solidarity and the progress of science, and who have even short runs of unused chemical periodicals, will communicate with the Comité Interamericano de Publicación Científica, Harvard College Observatory, Cambridge 38, Massachusetts.

Creep under Constant Load in Tension

PAUL J. BLATZ AND ARTHUR V. TOBOLSKY

Frick Chemical Laboratory, Princeton University, Princeton, New Jersey
January 11, 1946

ONE of the most commonly observed and measured of the phenomena pertaining to elastic-viscous behavior is creep under constant load. The simplest postulated elastic-viscous body, namely one which obeys Maxwell's equation, should exhibit a creep that is linear with time. It has been shown, however, that elastic materials that obey the kinetic theory of elasticity and are characterized by a single relaxation time, although they obey Maxwell's equation in shear, are governed by the following relation between stress, strain, and time for simple tensile deformations.¹

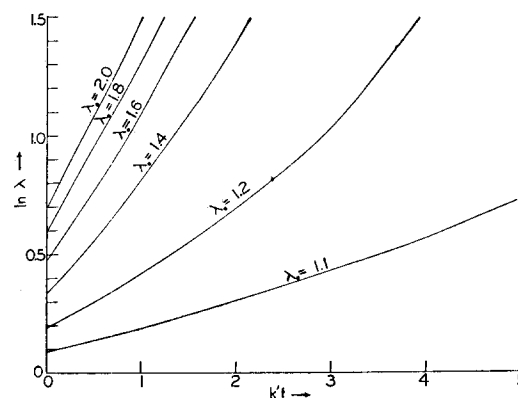


FIG. 1.

$$\frac{f}{cskT} = \exp(-k't) \left[\left(\frac{l(t)}{l_u} \right)^2 - \frac{l_u}{l(t)} \right] + \int_0^{k't} k' \exp[-k'(t-t')] \left[\left(\frac{l(t)}{l(t')} \right)^2 - \frac{l(t')}{l(t)} \right] dt', \quad (1)$$

where f is the stress on attained section at time t , s is the number of network chains of the elastic polymer per cc, k is Boltzmann's constant, T is the absolute temperature, k' is the relaxation rate, $l(t)$ is the length at time t , $l(t')$ the length at time t' , l_u the unstretched length, and c a constant.¹

If, as is often true, the volume of the elastic material is unchanged during stretching, the following relation obtains for an experiment for which a constant load is suspended on the material (creep under dead load).

$$\frac{f}{cskT} = \frac{l(t)}{l_u} \left[\frac{l_0}{l_u} - \left(\frac{l_u}{l_0} \right)^2 \right], \quad (2)$$

where l_0 is the initial length obtained immediately after the load is placed on the material. In other words, l_0 is the length attained by the sample under load due to the purely elastic response of the material before creep due to internal relaxation processes is observable.

If Eq. (2) is substituted into Eq. (1), the resulting equation may be transformed into a differential equation. For simplicity the following changes in notation were made:

$$\lambda = l(t)/l_u, \quad \lambda_0 = l_0/l_u, \quad \tau = k't.$$

The resulting differential equation is:

$$\frac{\lambda''}{\lambda'} = 1 + \frac{2\lambda'}{\lambda} - 2 \left(\frac{\lambda'}{\lambda} \right)^2 - \beta \frac{\lambda'}{\lambda^2}, \quad (3)$$

where

$$\beta = 3/(\lambda_0 - 1/\lambda_0^2)$$

and λ' and λ'' are first and second derivatives, respectively, with respect to t .

The solution of this equation was obtained by Laplace transformations giving:

$$\exp(k't) = P \left(\frac{2l}{\beta l_u} - 1 \right) + Q \left(\frac{2l}{\beta l_u} + 1 \right) \exp \left[-\beta \left(\frac{l_u}{l_0} - \frac{l_u}{l} \right) \right],$$

$$P = -\frac{\lambda_0^2 - 2\lambda_0 + 3}{\beta \lambda_0}, \quad (4)$$

$$Q = \frac{\beta}{2\lambda_0 + \beta} + \frac{2\lambda_0 - \beta}{2\lambda_0 + \beta} \cdot \frac{\lambda_0^2 - 2\lambda_0 + 3}{\beta \lambda_0}.$$

Graphs of this function in the form of $\ln l/l_u$ plotted against k/t are given (Fig. 1) for several values of l_0/l_u . It is particularly to be noted that the creep rate shows a very marked dependence on the load (as measured by the initial extension) even though the molecular relaxation is assumed independent of the stress. It should be remembered that these creep curves apply only to substances like the polysulfide rubbers² exhibiting a *single* relaxation time. Creep data obtained by Mr. Mochulsky on several polysulfide rubbers are in good agreement with the theory and will be published soon.

We wish to acknowledge the important mathematical advice we received from Professor V. Bargmann of the Institute for Advanced Study.

¹ M. S. Green and A. V. Tobolsky, J. Chem. Phys. **14**, 80 (1946).

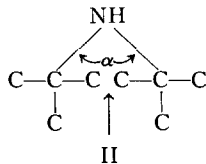
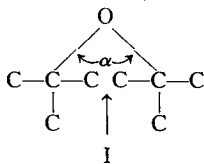
² M. D. Stern and A. V. Tobolsky, J. Chem. Phys. **14**, 93 (1946).

Steric Strain in Compounds with Tertiary Butyl Groups; Steric Strain in Polyisobutylene

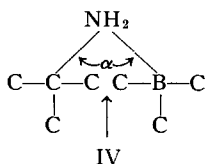
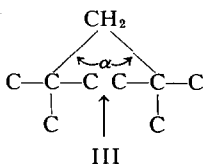
HERBERT C. BROWN AND GERALDINE K. BARBARAS

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January 11, 1946

COMPOUNDS containing two tertiary butyl groups attached to oxygen, nitrogen, or carbon, such as di-*t*-butylether, di-*t*-butylamine, and di-*t*-butylmethane, are characterized by difficulty of formation and relatively low stability. Examination of molecular models points to a considerable degree of steric interference (indicated by the arrow in I, II, and III) between the two tertiary butyl groups joined to the common atom.



This interference must result in a considerable increase in the bond angle α (I-III) from its preferred value and thereby lead to marked strain. In order to obtain an estimate of the strain, we have measured, by the experimental method previously reported,¹ the heat of dissociation of *t*-butylamine-trimethylboron (IV), a molecule whose structural skeleton and molecular dimensions are similar to those of the molecules under consideration.



It is not anticipated that the minor differences in the atomic radii of boron, carbon, nitrogen, and oxygen would bring about any major differences in the magnitude of the strain.

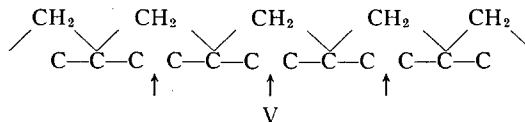
The dissociation constants for *t*-butylamine-trimethylboron between 50° and 90° are represented by the equation

$$\log K = -2850/T + 8.618.$$

The heat of dissociation of the compound is 13.0 ± 0.2 kcal. per mole.

Previous results have shown that where steric hindrance is not a major factor, the heat of dissociation of the addition compounds of trimethylboron with primary amines varies between the limits 17.6 and 18.4 kcal. per mole, with an average value of 18.0 kcal. per mole.² The steric strain in *t*-butylamine-trimethylboron may therefore be estimated to be in the neighborhood of 5 kcal. per mole.

This estimate receives interesting confirmation from the data reported by Evans and Polanyi³ for the heat of polymerization of isobutylene to polyisobutylene. The experimental value, 12.8 kcal. per mole, is some 9 kcal. below the value of 21.4 kcal. per mole calculated for a strain-free molecule. Examination of a scalar molecule for polyisobutylene (represented schematically by V) reveals that the strain in this molecule is similar both in kind and in degree to that postulated for the simpler substances, I-IV, with one noteworthy difference.



In the simpler molecules containing two tertiary butyl groups united to a common atom, each tertiary butyl group encounters steric interference on but *one* side (I-IV). In the polyisobutylene molecule, however, each unit corresponding to these tertiary groups encounters steric interference on *two* sides (the end groups are neglected in this discussion). It follows that the over-all strain per tertiary butyl unit in polyisobutylene should be twice that per tertiary butyl group in the simpler molecules, I-IV. In view of this consideration, the value of 9 kcal. per mole arrived at by Evans and Polanyi for the steric strain in polyisobutylene is in excellent agreement with the value of 5 kcal. per mole that our studies indicate to be present in *t*-butylamine-trimethylboron and related substances.

¹ Brown, Taylor, and Gerstein, J. Am. Chem. Soc. **66**, 431 (1944).

² Unpublished work of Brown and Taylor.

³ Evans and Polanyi, Nature **152**, 738 (1943).

The Absorption Spectrum of Metal-Ammonia Solutions

RICHARD A. OGG, JR.

Department of Chemistry, Stanford University, California
January 14, 1946

NEW experimental studies of the visible absorption spectrum of dilute solutions of alkali and alkaline earth metals in liquid ammonia reveal complications apparently not recognized by previous investigators. On cooling fairly dilute (some 10^{-3} molar) solutions of sodium and magnesium from room temperature to about -80°C , there is a very noticeable darkening, together with a