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

Herbert C. Brown and Geraldine K. Barbaras

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 rubbers[2] 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).

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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.
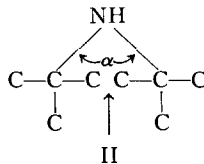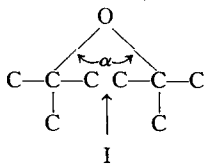
This interference must result in a considerable increase in the bond angle α (I–III) from its preferred value and thereby lead to marked strain. In order to obtain an estimate of the strain, we have measured, by the experimental method previously reported,[1] the heat of dissociation of *t*-butylamine-trimethylboron (IV), a molecule whose structural skeleton and molecular dimensions are similar to those of the molecules under consideration.
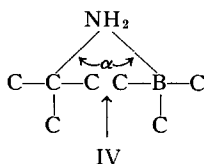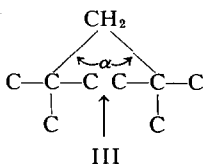
It is not anticipated that the minor differences in the atomic radii of boron, carbon, nitrogen, and oxygen would bring about any major differences in the magnitude of the strain.

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 Polanyi[3] 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.
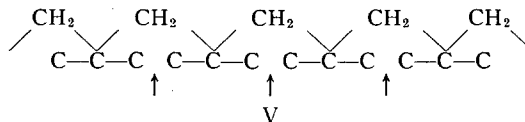
In the simpler molecules containing two tertiary butyl groups united to a common atom, each tertiary butyl group encounters steric interference on but *one* side (I–IV). In the polyisobutylene molecule, however, each unit corresponding to these tertiary groups encounters steric interference on *two* 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

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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

change in the quality of transmitted light. These phenomena are the more pronounced, the greater the concentration of the solution. The color change is rapid and completely reversible with respect to temperature change.

Quantitative spectrophotometric measurements confirm the qualitative visual observations as to change in color distribution of transmitted light. The absorption coefficient of a given solution for blue light is but slightly increased by the above temperature change, while that for red light is increased considerably—by a factor of two or more for sufficiently concentrated solutions. The change for light of intermediate wave-lengths falls smoothly between these extremes.

Previous studies[1, 2] have shown the absorption spectrum of very dilute metal-ammonia solutions to be continuous, with a pronounced maximum in the infra-red. Were this absorption band to undergo the normal broadening with temperature increase, the visible absorption spectrum would be affected in a fashion the reverse of that described above. The most probable interpretation of the present studies postulates the presence in the solutions of two different colored components, the equilibrium between these being dependent upon concentration and temperature. The component favored by high concentrations and low temperatures (which will be termed B) would appear to display also a continuous absorption spectrum, but with a band maximum lying nearer the visible region than that of the other component (which will be termed A). This would account for the observed differential increase of total absorption toward longer wave-lengths on cooling a relatively concentrated solution. The experimental results would indicate that the conversion of B into A is an endothermic process and must involve an increase in the number of particles.

Comparison with solid solutions of alkali metals in alkali halide crystals[3] affords a clue as to the difference between the A and B components. In these systems the F centers and F' centers (consisting, respectively, of single electrons and electron pairs trapped at vacant negative ion lattice sites) show different continuous absorption bands, the maximum of the F band lying at shorter wavelength. Absorption in both bands results in ejection of a conduction electron, the corresponding work function being greater for the F centers. Correspondingly, the F' centers are thermally unstable with respect to dissociation into F centers. In the present studies, it is suggested that the A component consists of single electrons trapped in cavities in the liquid dielectric medium[4] while the B component consists of electron pairs similarly trapped. However, the order of thermal stability of A and B components would appear to be reversed as compared with that of F and F' centers. Correspondingly, the positions on the wave-length scale of the corresponding band maxima are in all probability also reversed.

Theoretical treatment[4] of the electron pair trapped in a liquid medium of high dielectric constant predicts it to be stable with respect to dissociation into single electrons trapped in separate cavities, and that its ground state should be diamagnetic. The trapped single electron should have a paramagnetic susceptibility corresponding to electron spin. Experimental studies[5, 6] of the concentration and temperature dependence of the magnetic susceptibility of dilute metal-ammonia solutions are at least qualitatively explained by the above proposed equilibrium between trapped pairs and trapped single electrons. However, in attempting to calculate equilibrium constants from the magnetic data, it should be noted that the cavities occupied by both are very large[4] (of the order of 7×10^{-8} cm in radius) and that consequently the diamagnetic susceptibilities are far from negligible. The absorption spectrum studies offer hope of greater accuracy.

[1] G. E. Gibson and W. L. Argo, J. Am. Chem. Soc. 40, 1327 (1918).
[2] E. Vogt, Zeits f. Electochemie 45, 597 (1939).
[3] For literature references, see N. F. Mott and R. W. Gurney, Electronic Processes in Ionic Crystals (Oxford Press, 1940).
[4] Richard A. Ogg, Jr., J. Am. Chem. Soc (January, 1946), in press.
[5] E. Huster, Ann. d. Physik 33, 477 (1938).
[6] S. Freed and N. Sugarman, J. Chem. Phys. 11, 354 (1943).

Copolymerization of Systems Containing Three Components

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IN a previous letter[1] on this subject, we presented equations for the composition of the initial copolymer formed from a given mixture of 3 monomers, (A, B, and C).[2]

$$\frac{a}{b} = \frac{[\beta^a \gamma^b AB + \gamma^a \beta^a A^2 + \gamma^a \beta^c AC]}{[\alpha^b \gamma^a AB + \gamma^b \alpha^b B^2 + \gamma^b \alpha^c BC]} \cdot \frac{[A + \alpha^b B + \alpha^c C]}{[B + \beta^a A + \beta^c C]}, \quad (1)$$

$$\frac{a}{c} = \frac{[\beta^a \gamma^b AB + \gamma^a \beta^a A^2 + \gamma^a \beta^c AC]}{[\alpha^c \beta^a AC + \beta^c \alpha^b BC + \beta^c \alpha^c C^2]} \cdot \frac{[A + \alpha^b B + \alpha^c C]}{[C + \gamma^a A + \gamma^b B]}. \quad (2)$$

Here a, b, and c are molar concentrations of the three components in the initial polymer; A, B, and C are the molar concentrations in the monomer mixture; α^b, α^c, —, etc. are ratios of propagation rate constants, as follows:

$$\alpha^b = k_{ab}/k_{aa}, \qquad \beta^a = k_{ba}/k_{bb}, \qquad \gamma^a = k_{ca}/k_{cc},$$
$$\alpha^c = k_{ac}/k_{aa}, \qquad \beta^c = k_{bc}/k_{bb}, \qquad \gamma^b = k_{cb}/k_{cc}.$$

It was stated that "equations 1 and 2 indicate the possibility of predicting the composition of a multipolymer from information gathered from a separate study of each pair of monomers involved." This is, in general, true. Dr. G. L. Barrett[3] has pointed out, that there is an important class of monomers for which such a calculation is impossible. Members of this class (e.g., maleic anhydride, maleic esters) possess vanishingly small rate constants for self-propagation.[4] If monomer C in a 3-component polymerization is of this type, then k_{cc} is equal to zero; γ^a and γ^b are infinite. The structure of the tripolymer depends upon all 9 of the propagation constants. In the usual case, where no constant vanishes, knowledge of the six ratios used in Eqs. (1) and (2) means implicit knowledge of all other necessary ratios. Thus (k_{ca}/k_{cb}) is fixed if the ratios (k_{ca}/k_{cc}) and (k_{cb}/k_{cc}) are known. If k_{cc} vanishes, however, experiments on the separate 2-com-