of the peroxide disappears by another primary reaction (such as heterolytic fission, intramolecular decomposition or electron transfer reactions involving solvent) the measured activation energies would have to be interpreted differently. While such reactions have been suggested there are, as far as the author is aware, no conclusive data showing that they must be considered under conditions such as those used here.

Acceptance of the kinetic data as giving a measure of the dissociation energy leads to a value of about 29 kcal./mole for this quantity in alkyl hydroperoxides. This value compares with 31.7 and 36.0 kcal./mole for diethyl peroxide and di-*t*-butyl peroxide which have been determined by apparently unambiguous kinetic methods by Rebbert and Laidler[19] and Murawski, Roberts and Szwarc,[20] respectively. The dissociation energy of 52 kcal./mole for hydrogen peroxide, determined from thermodynamic measurements,[21] however, is considerably greater.

The large difference in the dissociation energies of hydrogen peroxide and the dialkyl peroxides has been pointed out by Rebbert and Laidler.[19] Bell, Raley, *et al.*, found the dissociation energy of *t*-butyl hydroperoxide to be the same as di-*t*-butyl peroxide and have commented upon this surprising coincidence in view of the hydrogen peroxide value.[10] The similarity between the dissociation energies of alkyl hydroperoxides and dialkyl peroxides, if the values are real, would indicate that the alkyl substituents have no pronounced effect upon the peroxide bond nor upon the resonance stabilization of the $XO\cdot$ radical which would be required to account for the effect of alkyl substitution in lowering the hydrogen peroxide dissociation energy.

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[19] R. E. Rebbert and K. J. Laidler, *J. Chem. Phys.*, **20**, 574 (1952).

[20] J. Murawski, J. S. Roberts and M. Szwarc, *ibid.*, **19**, 698 (1951).

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COMMUNICATIONS TO THE EDITOR

ON THE NATURE OF THE STRUCTURAL ELEMENT OF COLLAGEN

Sir:

The reconstitution of collagen fibrils from acid solutions of collagenous tissue[1] has created considerable interest in the nature of the dispersed units in such solutions. Moreover, the periodicities observed in electron micrographs[1,2,3] suggest that the different fibrous forms of collagen have a common building unit of macromolecular size. To date investigations of these dispersed units have led to wide disagreement on the molecular or particle weight, values near 70,000[4,5] and in the range 1.7 to 24 million[5,6,7] having been reported. This and the corresponding lack of agreement about size and shape suggest that the fundamental dispersed unit in solution has not yet been defined. We wish to summarize evidence demonstrating that these units are rigid, rod-shaped particles having a very narrow size distribution and the following approximate characteristics: diameter, 14 Å. (hydrated); length, 2900 Å; weight, 300,000.

We have employed citrate extracts of ichthyocol from tunics of carp swim bladder[7,8] throughout and our results are the same for different tunics, successive extracts of the same tunics and successive precipitations of the same preparation. With respect to particle weight, we found 340,000 ± 50,000 by light scattering; 300,000 ± 50,000 by osmotic pressure; 300,000 ± 20,000 from sedimentation constant (2.85×10^{-13}) and intrinsic viscosity (11.5) assuming 34% hydration and a high axial ratio,[9] and 300,000 ± 20,000 from flow birefringence assuming 34% hydration and a cylindrical form with a diameter of 14 Å. obtained from the sedimentation constant. The close agreement between the values obtained here, particularly the light scattering and osmotic pressure, together with the narrow range of size observed in flow birefringence (2500–2900 Å. lengths),[10] demonstrate the unusual narrowness of the particle size distribution.

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[1] See review by R. S. Bear, "Advances in Protein Chemistry," **7**, 69–160, Academic Press, Inc., New York, N. Y., 1952.

[2] F. O. Schmitt, J. Gross and J. H. Highberger, *Proc. Natl. Acad. Sci.*, **39**, 459 (1953).

[3] J. Gross, J. H. Highberger and F. O. Schmitt, *ibid.*, **40**, 679 (1954).

[4] S. E. Bresler, *et al.*, *Reports Acad. Sci. U.S.S.R., Moscow*, **72**, 555 (1950).

[5] M. B. Mathews, E. Kulonen and A. Dorfman, *Arch. Biochem. and Biophys.*, **52**, 247 (1954).

[6] M. B. M'Ewen and M. I. Pratt, pp. 158–168, in J. T. Randall (ed.), "Nature and Structure of Collagen," Academic Press, Inc., New York, N. Y., 1953.

[7] P. M. Gallop, *Biochem. and Biophys. Acta*, in press; thesis, Massachusetts Institute of Technology, Cambridge, Mass., 1953. The sedimentation constant and intrinsic viscosity of our preparations agreed with those of Gallop.

[8] The absence of contamination of our materials by parent gelatin was evident from the solubility behavior, the fibrous nature of precipitates and the specific rotation of −350° established by Dr. Carolyn Cohen (Ph.D. thesis, M.I.T., 1954) for purified ichthyocol extracts.

[9] H. A. Scheraga and L. Mandelkern, THIS JOURNAL, **75**, 179 (1953).

[10] This range of particle lengths is that required to represent the extinction angle data from 0–6000 sec.$^{-1}$. This is a highly weighted average and consequently defines fairly well the upper but not the lower limit of the size distribution.

To obtain reproducible light scattering values, it was necessary to avoid exposing the solutions to temperatures above 20° and to centrifuge at concentrations *below 0.2%* at 40,000 *g* for several hours. Centrifugation at higher concentrations yielded light scattering values as much as double that reported above but the other measurements remained essentially unchanged. This behavior is consistent with the existence of a very small fraction of the solute in the form of side-by-side aggregates. This may account in part for the much higher values obtained by others using this method.

Evidence for the shape of the particle can be obtained from the shape of the reciprocal scattering envelope now that polydispersity has been shown to be low. These data are matched within 5% by the envelope of a rod-shaped particle of 3000 Å. length. The intrinsic viscosity yields an axial ratio of 170. In this range the sedimentation constant is almost entirely dependent on diameter and corresponds to 17 Å. for an ellipsoid, 14 Å. for a cylinder. This leads to an ellipsoid length of 2900 Å. In addition to the above mentioned flow birefringence data, based on extinction angle measurements, the variation of the specific birefringence with gradient was characteristic of that of a rod. Finally, the absence of a polyelectrolyte effect in the reduced specific viscosity upon lowering the ionic strength insured the rigidity of the rod-like particle.

Inasmuch as this particle appears to embody the essential characteristics of a building unit postulated by Schmitt, Gross and Highberger[2,3] from which the three different structural forms of collagen are formed, it may be proper to give it the name tropocollagen suggested by these authors.

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RECEIVED NOVEMBER 26, 1954

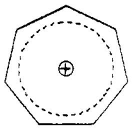
THE VIBRATIONAL SPECTRUM AND STRUCTURE OF THE TROPYLIUM ION

Sir:

Doering and Knox[1] have recently prepared cycloheptatrienylium (tropylium) bromide and obtained chemical and physical properties which indicate that the tropylium ion represents a new aromatic system the relative stability of which is due to resonance resulting from the presence of six (π) electrons in the conjugated unsaturated seven membered ring. As part of a program of studying the Raman spectrum of colored substances we have obtained the Raman spectrum of tropylium bromide and we wish to give here a preliminary report of the vibrational spectrum of the tropylium ion. This spectrum supports the conclusion of Doering and Knox that this ion represents a new aromatic system.

The Raman spectra were obtained on a Hilger E 612 Spectrograph having a camera aperture of F 5.4 and using Hg 5461 Å. excitation. Because of the photochemical reactivity of the tropylium ion, extremely heavy optical filtering was required to eliminate all blue radiation from the sample. The filters used were saturated K_2CrO_4 and $NdCl_3$ solutions and a Kodak Wratten #55 filter. The spectra were obtained in 25% hydrobromic acid solution, and a typical concentration of tropylium bromide in this solution was about 1 mole/liter. As with ferrocene it was found that an optimum concentration exists for obtaining the maximum intensity of scattered radiation at a given wave length.[2] There was no photochemical decomposition of the sample under prolonged exposure to Hg 5461 Å. radiation. Infrared spectra were obtained in HBr solution and KBr pellet using a Perkin-Elmer model 12c Spectrometer. The infrared spectrum in a KBr pellet has been reported by Doering and Knox.[1] The Raman and infrared spectra in HBr solution are collected in Table I. The observed Raman and infrared frequencies of benzene corresponding to the allowed fundamental modes of vibration are also given for comparison.

A study of the vibrational spectrum of the tropylium ion reveals the following features: (1) The Raman and infrared spectrum are remarkably simple for a system having thirty-six vibrational degrees of freedom, indicating a structure of high symmetry. (2) There are no coincidences between Raman and infrared frequencies, indicating a structure of high symmetry. (3) The position, distribution and relative intensities of the observed frequencies are readily interpreted in terms of an aromatic system, and there is good correlation with the corresponding frequencies of benzene. These features are all consistent with a planar aromatic structure having D_{7h} symmetry.



The selection rules for such a structure predict no coincidences with seven Raman ($2A_1'$, $1E_1''$, and $4E_2'$) and four infrared ($1A_2''$, and $3E_1'$) active fundamentals. These numbers agree remarkably well with the observed spectrum of seven Raman lines and four relatively strong infrared peaks. The two totally symmetric A_1' fundamentals are readily assigned to the 868 cm.$^{-1}$ and 3065 cm.$^{-1}$ Raman lines as the ring breathing and C–H stretching modes, respectively. Their intensity and appearance indicate that they are probably polarized as expected from the selection rules. A comparison of the spectrum of tropylium ion with that of benzene shows a number of expected similarities. In the Raman spectrum the C–H stretching frequencies appear at 3065 cm.$^{-1}$, the C–H in plane bending frequencies appear near 1200 cm.$^{-1}$, and the C–H out of plane bending near 900 cm.$^{-1}$, all quite close to the corresponding frequencies in benzene. Of the Raman active skeletal frequencies one

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(1) W. von E. Doering and L. H. Knox, THIS JOURNAL, **76**, 3203 (1954).

(2) E. R. Lippincott and R. D. Nelson, *J. Chem. Phys.*, **21**, 1307 (1953).