



FIG. 1. Induction times vs inverse temperature. This work, —; Schott and Kinsey, - - - - -.

duction periods in a manner which suggested a branching chain mechanism closely analogous to that proposed for the hydrogen-oxygen reaction.² Details of this mechanism have been discussed.^{1,3}

A series of experiments using the x-ray densitometric technique⁴ was undertaken to determine the relationship of the chemiluminescence to the heat evolution of the reaction. The apparatus employed was described previously.⁵ A mixture was prepared consisting of 96.61% xenon, 1.35% acetylene, and 2.04% oxygen. It was intended that the experimental conditions be nearly the same as those employed in the chemiluminescence studies, which meant that the starting pressures were considerably lower than in previous work with the x-ray densitometric technique. The conditions of eight incident shock waves are given in Table I.

Due to the low concentration of x-ray absorber, the signal-to-noise ratio of the oscilloscope records was too low for quantitative density measurements. The qualitative appearance of the records was as follows. The sudden increase in density in the incident shock wave was followed first by a short period of constant density and then by a slow decrease to a somewhat lower density, which remained constant thereafter until the arrival of the contact surface. The decrease in density can be attributed unambiguously to release of heat in the approach to final equilibrium. To obtain a value for the induction time from a density record, straight lines were drawn through the initial constant density level and the following decrease, and the intersection taken to be the end of the induction period. The time elapsed between the passage of the shock and the end of the induction period was multiplied by the value of the density ratio of the incident shock calculated from

the shock velocity to obtain the length of the induction period in gas time. Table I lists the results obtained.

The mechanism proposed^{1,3} for the branching chain reactions governing the induction period in this reaction predicts that the product of oxygen atom concentration and induction time plotted logarithmically against inverse temperature should yield a straight line. This is shown in Fig. 1. Least-squares analysis of the results yields the value 19.0 kcal for the activation energy of the rate controlling step of the reaction, with a standard error of estimate of 2.6 kcal at 50% confidence level.

Since the results of the chemiluminescence experiments yield similar values for the induction periods, it is clear that the emission of ultraviolet light starts at about the same time as the release of heat. The implications of this are discussed elsewhere.^{1,3} The induction times obtained mass spectrometrically at lower temperatures scatter uniformly about the extrapolated solid line.³ The striking correlation of the acetylene-oxygen and hydrogen-oxygen² induction periods can be seen in the close agreement of the two least squares lines shown in Fig. 1.

This work was supported by the Office of Naval Research.

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Zero-Point Vibrations in Benzene

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(Received July 18, 1961)

THIS note is written to point out some elementary but interesting conclusions about benzene, which one can draw from just a little well-known information: the vibration frequencies of the two B_{2u} modes of the benzene molecule, and the currently popular values for "natural" single and double bonds between trigonal carbon atoms. Mair and Hornig¹ report the vibrational frequencies ν_{14} and ν_{15} as 1310 and 1150 cm^{-1} , respectively; Scherer and Overend have substantiated this assignment from their examination of the Urey-Bradley force field.² Carbon-carbon bond lengths have been much discussed; a summary of recent literature is included in an article by Bernstein.³

We shall suppose the double- and single-bond lengths appropriate to a hypothetical cyclohexatriene molecule

are 1.335 and 1.465 Å, respectively; these are probably not in error by more than 0.01 Å. We note that within 0.003 Å, these bond lengths make it possible for benzene to attain the cyclohexatriene structure by a distortion only along the B_{2u} symmetry coordinate S_{14} , in the notation of Wilson *et al.*⁴ This symmetry coordinate corresponds to stretching and shrinking alternate C—C bonds around the ring.

First, what energy is necessary to distort benzene into our chosen "cyclohexatriene" structure? This question was examined by Hornig⁵ who used 1.54 Å as his chosen single-bond length. We find that the reduction of this figure to 1.465 makes a drastic difference in the conclusions. From the analysis of Crawford and Miller,⁶ Hornig found that the force constant for the S_{14} symmetry coordinate is 4.361 or 3.926×10^5 d/cm. Let us treat this as if it were a true harmonic force constant to estimate the energy difference between the equilibrium configuration of benzene and our chosen cyclohexatriene structure. We find readily that with

$$S_{14} = 6^{-\frac{1}{2}} \times 0.065 \times 6,$$

the total energy of distortion is only 7.92 or 7.14 kcal/mole.

By comparison, the zero-point energy of the higher frequency B_{2u} mode, which is principally composed of the S_{14} symmetry coordinate vibration, is 1.87 kcal. The cyclohexatriene structure, therefore, has an energy between that of the first and second excited states of the ν_{14} vibrational degree of freedom.

We can also inquire into the magnitude of the displacement associated with achieving the cyclohexatriene structure. The displacement, measured in classical amplitudes, is $(7.92/1.87)^{\frac{1}{2}}$ or $(7.14/1.87)^{\frac{1}{2}}$, or 2.06 or 1.95, respectively. Continuing to treat the vibration as a harmonic mode and examining the area under a $|\psi|^2$ curve, we conclude that benzene in its ground vibrational state spends about 15% of its time at least as distorted as our hypothetical cyclohexatriene molecule.

Finally, we estimate that if a force constant of 4.361 or 3.926×10^5 d/Å is associated with a vibration whose natural frequency is 1310 cm^{-1} , then the classical zero-point amplitude of motion for a carbon atom in this mode is 0.031 or 0.033 Å, which is a surprisingly large figure.

The question arises immediately as to the origin of such large-amplitude, low-energy motion. A suggestion was made by the author,⁷ in connection with the distorted rings of crystalline dibenzene chromium, that the π electrons are not the major source of stability for the regular hexagon, and that in fact the π electrons might well have a lower energy if the rings approach "cyclohexatriene"-like shapes. This would imply that the π electrons are largely responsible for the ease of distortion, and that the σ electrons determine the regular hexagon structure. Snyder⁸ has carried out

Hückel model calculations of π and σ contributions to the energy of the B_{2u} distortion of benzene, and concludes that this is indeed the case. The numerical values of the contributions are sensitive to the exact form of the potential. Nonetheless, two rather different potentials, those of Lennard-Jones⁹ and of Longuet-Higgins and Salem¹⁰ both show the π electrons to be contributing to the *instability* of the regular hexagon of benzene, and therefore to the large-amplitude motion.

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Electron Spin Resonance Measurements of Preferred Orientation in Quickly Frozen Hydrogen Peroxide Solutions*

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(Received August 23, 1961)

THE free radicals produced by the ultraviolet irradiation of $\text{H}_2\text{O}_2\text{—H}_2\text{O}$ solutions can be stabilized at low temperatures and detected in this state by electron spin resonance (ESR).^{1,2} The measurements reported here use the ESR spectrum obtained from these radicals to determine the distribution of crystallites within a frozen sample.

The solutions were put into quartz glass tubes of 2–3 mm i.d. and then frozen by plunging the tubes into liquid oxygen. 97% w/w $\text{H}_2\text{O}_2\text{—H}_2\text{O}$ produced a polycrystalline material³ and this was used for the first experiments.

The material was tested to see if there was any preferred orientation of the crystallites to the tube axis. A tube was constructed of three pieces so that the middle section of 5 mm length could be removed after the solution had frozen. This section was irradiated at 90°K with the light falling perpendicular to the tube