Electron Spin Resonance of Cyclopentadienyl

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packed balls was tested for its behavior under shearing with the aid of a box constructed with hinged end plates and walls dimpled to prevent initiation of regular packing at the surfaces. The box was partially filled with about 16 000 $\frac{1}{8}$-in. steel balls. Oscillating the coupled end plates immediately showed that such an assembly has no significant resistance to shearing. In contrast to the rigidity of regular packing, randomly packed spheres are quite fluid.

A shearing experiment was carried out by filling the box with balls in random *loose* packing and then noting the volume change after repeated shearings through a selected angle. The volume decreased rapidly at first but after about 100 oscillations reached a constant characteristic of the maximum shear angle. The limiting *mean* packing density of the assembly corrected for peripheral error is shown as a function of maximum shear angle in Fig. 2. The mean densities above the random close packing limit indicate the presence of regions of *regular* packing, which grew as "crystals" in the "liquid." If the shearing is considered analogous (albeit in a remote way) to thermal agitation then the occurrence of the regular packings over the 15°–30° shearing angle may be thought of as the liquid–solid transition which normally takes place only over a limited temperature range.

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Electron Spin Resonance of Cyclopentadienyl

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IT was found that pyrolysis of a molecular beam of dicyclopentadienyl iron (ferrocene) leads to formation of cyclopentadienyl radicals.

The method employed presently to generate and trap the radical has been described previously[1] and, therefore, only a few details are mentioned here. Ferrocene is evaporated in vacuum and passed through a hot furnace. For furnace temperatures above 800°C, dissociation occurs and the gas mixture consisting of undecomposed ferrocene and radical is condensed on a cold trap maintained at liquid-nitrogen temperature.

The second derivative of the observed electron spin resonance absorption spectrum consists of six equally spaced lines with a splitting of 5.98 G. The intensity ratio is 1:5:10:10:5:1, characteristic for five equivalent protons. The value of Q, assuming carbon spin densities of $\frac{1}{5}$ is $Q=29.9$ G.

In cyclopentadienyl, the pentagonally symmetrical structure is not stable and the radical distorts to give a symmetry D_{2h}. Calculations have shown that two distorted structures should exist of nearly the same energy.[2] The spectrum indicates that an averaging over the two conformations takes place leading to the equivalence of the five protons.

At lower temperatures, stable radicals of D_{2h} symmetry might occur. However, anisotropic broadening can be expected to make the observation of hyperfine structure impossible.

It seems worth mentioning that pyrolysis of azobenzene ($C_6H_5NNC_6H_5$) leads to the same radical. Presumably some of the azobenzene dissociates into C_5H_5 and CN, in close analogy with the dissociation of hydrazobenzene ($C_6H_5NNC_6H_5$) where C_5H_5 and HCN are formed.[3]

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Direct Photolysis of Ethane at Low Conversions*

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RECENT investigations of both the radiolysis[1–3] and direct photolysis[4] of gaseous ethane have brought to the fore the occurrence of a primary process involving molecular detachment of hydrogen

$$C_2H_6 \rightarrow CH_3CH + H_2 \qquad (1)$$
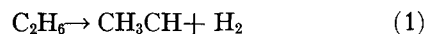
uninfluenced by the presence of hydrogen-atom scavengers. The contribution of (1) to primary radiolytic decomposition was effectively established[2,3] at $\sim$37% by following the rate of hydrogen formation at conversions as low as $10^{-3}\%$. By means of a similar procedure, mercury-photosensitized decomposition of ethane was found[5] to be initiated almost entirely by radical formation:

$$C_2H_6 \rightarrow C_2H_5 + H. \qquad (2)$$
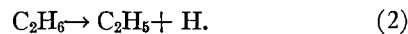
Observed decreases in over-all hydrogen-production rates in going to higher conversions were ascribed to reaction of hydrogen atoms with ethylene as they appeared following rearrangement of CH_3CH radicals and/or disproportionation of ethyl radicals. At room
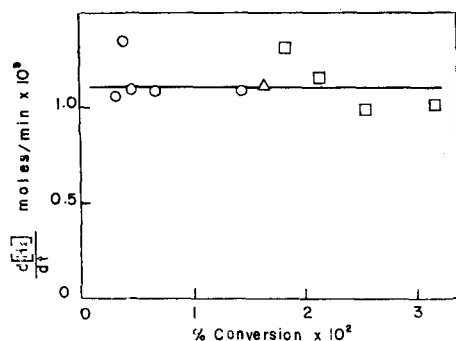
FIG. 1. Hydrogen formation in direct photolysis of ethane. O, research grade; □, purified[5]; △, 5 mole % C_2H_4 added.

temperature the ethylene reached steady-state abundances very early in the decomposition ($\sim 2 \times 10^{-3}\%$ in radiolysis[3]).

Direct photolysis of ethane in a static system at gross conversions of $10^{-2}\%$ and higher revealed no significant contribution by radical process (2).[4] Since 1470-Å light is absorbed[6] in only a few tens of microns at ~ 10 mm Hg, occurrence of (2) may have been obscured by localized high conversions near the lamp window. The results reported here are those of experiments aimed at low conversions in direct photolysis by means of rapid gas flow past the lamp window. With flow rates up to 2×10^{-4} moles/min at ~ 10 mm Hg, it was possible to achieve conversions as low as $4 \times 10^{-4}\%$.

Phillips research-grade ethane, purified by exposure to bromine[5] and subsequent fractional distillation in a LeRoy still,[7] was used in some runs. A low-pressure xenon arc lamp excited by a Raytheon Model CMD-10 microwave power supply provided 1470-Å light through two LiF windows separated by a vacuum or filter chamber. Unidirectional gas flow was maintained by freezing "spent" ethane at $-210°$. Noncondensables at $-196°$ were collected and analyzed mass spectrometrically. No methane was observed over the residual $\sim 5 \times 10^{-4}\%$ remaining from the purification.

Figure 1 summarizes the results of several irradiations at room temperature. Consistent with the precision attained, the hydrogen-production rate is seen to be independent of the extent of conversion in the range studied. Irradiation of untreated research grade ethane, known[3] to contain ethylene at about 10^{-3} mole %, gave the same rate of hydrogen formation. Similarly, no decrease was observed upon addition of ethylene at a concentration of 5 mole %, sufficient to scavenge all hydrogen atoms.

The results of Fig. 1 thus show no evidence for hydrogen-atom formation and permit setting a lower limit of about 80% on the extent of molecular detachment in direct photolysis.[8] One encounters, in this system, an excited state not readily converting to the lower energy state associated with C–H bond rupture as in mercury photosensitized decomposition of ethane. In contrast, direct photolysis of methane[9] at 1249 Å

exhibits significant contribution by primary C–H bond split to give hydrogen atoms.

The study of direct photolysis of ethane awaits measurement of all significant decomposition products whose relative amounts may provide further indications of the roles of the primary processes.[10]

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On the Correlation Energy in the CH_4 Molecule

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IN recent papers Nesbet and Clementi reported a value for the molecular extra correlation energy in the HF molecule.[1] By assuming this energy to be equal to the correlation energy for the electron pair forming a C–H bond in CH_4, Clementi has also been able to give a value for the total correlation energy in this molecule.[2]

The purpose of this note is to examine a different method for estimating the correlation energy in the CH_4 molecule. This method is based solely on atomic correlation energy data, and does not imply any assumption concerning the electronic correlation in other molecules. It extends Nesbet's method of comparing molecular correlation to that of ions as done for HF.

We assume that the C–H bonds in CH_4 are described by strictly localized electron pairs occupying orbitals having strongly directional character, and describing the valence state of the C atom in the molecule. Following Clementi we assume the wavefunction for the $1s$ electrons to be unperturbed by the rearrangements induced in the valence shell by the transformation of the C atom to the appropriate valence state. The estimated correlation energy for the inner shell electrons in the free C atoms therefore can be carried over to the discussion of CH_4 in this approximation.