

## Electronic Structure of Ferrocene

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The total  $\pi$ -electron energies calculated by the two approximations also agree very closely. As expected, the ASMOCI procedure yields a slightly lower energy in each case.

Full details of the calculations will be reported elsewhere. One of us (A.P.) acknowledges the award of a CSIRO studentship.

- <sup>1</sup> Lennard-Jones, Proc. Roy. Soc. (London) **A198**, 1, 14 (1949).  
<sup>2</sup> Hall, Proc. Roy. Soc. (London) **A205**, 541 (1951).  
<sup>3</sup> C. C. J. Roothaan, Revs. Modern Phys. **23**, 69 (1951).  
<sup>4</sup> Pople, Trans. Faraday Soc. **49**, 1375 (1953).  
<sup>5</sup> R. Pariser and R. G. Parr, J. Chem. Phys. **21**, 466, 767 (1953); **23**, 711 (1955).  
<sup>6</sup> Skinner and Pritchard, Trans. Faraday Soc. **49**, 1254 (1953).  
<sup>7</sup> Kotani *et al.*, J. Phys. Soc. Japan **8**, 463 (1953).  
<sup>8</sup> Roothaan, "Tables of Two-Center Coulomb Integrals between 1S, 2S, and 2P Orbitals," (University of Chicago, Physics Department, Office of Naval Research Report, 1955).

### Mechanism of the Decomposition of Primary and Secondary *n*-Butyl Free Radicals

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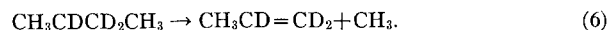
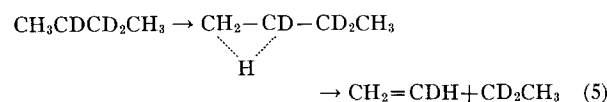
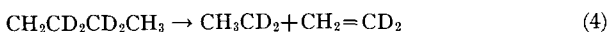
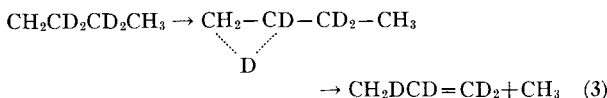
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THE decomposition of the *n*-butyl radical produces ethylene and propylene as major products. The mechanism for production of these products has been investigated by the photolysis and pyrolysis of acetone in the presence of *n*-butane-2, 2, 3, 3-*d*<sub>4</sub>. Butyl radicals are produced by the reactions:

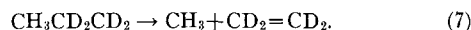


The butyl radicals formed in (1) and (2) decompose to form smaller radicals and an olefin. This breakdown is possible because most of the energy required to break the carbon-carbon bond is recovered by the formation of a double bond.

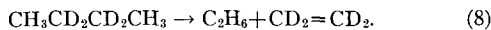
Two possible mechanisms may be formulated for the breakdown of each of the *n*-butyl radicals.



In addition, any *n*-propyl radicals formed on the wall would decompose in part by



Ethylene-*d*<sub>4</sub> could also be formed by the intramolecular reaction



The marking of the olefin products reveals the mechanism of their formation.

I. A 2:1 mixture of acetone and *n*-butane-2,2,3,3-*d*<sub>4</sub> whose total pressure was 32 mm was heated in a 50-ml fused silica reaction vessel at 506° for four minutes. The reaction had proceeded only a few percent toward completion. The propylene and ethylene fractions were separated from the reaction mixture by means of vapor phase chromatography, using a 6-ft carbon black (Pelletex) column containing 1.5% Octoil-S. The fractions were analyzed for purity and isotopic composition on the mass spectrometer. The propylene fraction revealed a maximum mass at 45. Less than one percent of this amount appeared at mass 46. No propane was formed in the pyrolysis reaction. The propylene is almost ex-

clusively propylene-*d*<sub>3</sub>. Unfortunately, the ethylene fraction was contaminated with ethane and nothing can be said regarding its isotopic composition.

II. A 1:4 mixture of acetone and *n*-butane-2,2,3,3-*d*<sub>4</sub> was similarly photolyzed for 30 minutes at 365° using a medium pressure mercury arc. A 50 ml sample of the reaction mixture at 30 mm pressure was again subjected to vapor phase chromatography. A 10 ft carbon black (Pelletex) column containing 1.5% squalane was used to facilitate propylene-propane separation, since propane is a product in the photolysis. Again the propylene was almost entirely propylene-*d*<sub>3</sub>. The ethylene fraction was uncontaminated with ethane and had its maximum appreciable mass at 30. One percent of this amount appeared at mass 31. Further, the mass spectrum of the ethylene fraction was identical with that of the ethylene obtained from the room temperature photolysis of  $\alpha,\alpha'$  diethyl ketone-*d*<sub>4</sub>.<sup>1</sup> The mechanism of the ethylene formation from this reaction<sup>2,3</sup> has been shown to be



The absence of  $\text{CD}_2 = \text{CD}_2$  eliminates reactions (7) and (8). The above evidence also shows that little or no  $\text{CH}_2 = \text{CHD}$  is formed. In the pyrolysis, the  $\text{CH}_3\text{CD}_2$  radical can decompose to a limited extent. Since this reaction produces the same type of ethylene as reaction (4), it cannot affect the conclusions regarding decomposition of the *n*-butyl radical.

Secondary *n*-butyl radicals, therefore, cannot produce ethylene as suggested by reaction (5). The absence of propylene-*d*<sub>4</sub> from 365–506° likewise eliminates reaction (3) as a possible source of propylene.

It may be concluded that (1) hydrogen atoms cannot be transferred intramolecularly from one carbon atom to another in the *n*-butyl radical, and (2) that no ethylene is formed by the intramolecular decomposition of butane under the conditions of the experiments.

- <sup>1</sup> McNesby, Drew, and Gordon, J. Phys. Chem. **59**, 988 (1955).  
<sup>2</sup> M. H. J. Wijnen and E. W. R. Steacie, Can. J. Chem. **29**, 1092 (1951).  
<sup>3</sup> Kutschke, Wijnen, and Steacie, J. Am. Chem. Soc. **74**, 714 (1952).

### Electronic Structure of Ferrocene

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 (Received March 9, 1956)

RECENTLY, E. A. Seibold and L. E. Sutton<sup>1</sup> measured the Fe–C (2.03 Å) and C–C (1.43 Å) distances of ferrocene [ $\text{Fe}(\text{C}_5\text{H}_5)_2$ ] and ascertained the highly symmetrical "sandwich" structure proposed by Wilkinson *et al.*<sup>2</sup> We treat this molecule by a simplified SCF LCAO–MO theory.<sup>3</sup> As a result, the closed shell ground state and the nearly free rotation of two cyclopentadienyl rings are concluded, and three transitions are anticipated, 0.9 ev, 2.5 ev, and 3.7 ev, being compared with the experimental values 2.82 ev and 3.43 ev.<sup>2</sup>

The following are used. (1) The overlaps of AO's are neglected. (2) Inner 18 electrons of Fe and 2 1s electrons of each carbon make inner cores, and 15 2s electrons of a C–ring, with 5 1s electrons of H, make a pentagonal skeleton. These screen the nuclei perfectly. (3) Ten 2p electrons of C–rings and 8 3d, 4s electrons of Fe are considered and Slater functions<sup>4</sup> are used ( $\zeta_{\text{C } 2p} = 1.590$ ,  $\zeta_{\text{Fe } 3d} = 2.200$ ,  $\zeta_{\text{Fe } 4s} = 0.878$ ).

From 10 2p AO's  $\phi_1', \phi_2', \dots, \phi_5', \phi_1'', \phi_2'', \dots, \phi_5''$  of 2 rings the ligand orbitals  $\rho_0^+, \rho_0^-, \rho_1^+, \rho_1^-, \rho_{-1}^+, \rho_{-1}^-, \rho_2^+, \rho_2^-, \rho_{-2}^+, \rho_{-2}^-$  are made as follows:

$$\rho_0^\pm = \rho_0' \pm \rho_0'' \quad \rho_{(-)1}^\pm = \rho_{(-)1}' \pm \rho_{(-)1}'' \quad \rho_{(-)2}^\pm = \rho_{(-)2}' \pm \rho_{(-)2}''$$

with

$$\begin{aligned} \rho_0^{r'''} &= (1/5)^{1/2} \sum_r \phi_r^{r'''} \quad \rho_{(-)1}^{r'''} = (1/5)^{1/2} \sum_r \exp\{(-i)r\theta\} \phi_r^{r'''} \\ \rho_{(-)2}^{r'''} &= (1/5)^{1/2} \sum_r \exp\{(-2ir)\theta\} \phi_r^{r'''} \end{aligned}$$

The Mo's  $\psi_i$  are linear combinations between ligand- and Fe metal-orbitals. Combining relations are decided by the symmetry  $D_{5h}$  of the molecule. Electron repulsion integrals are neglected except  $\gamma_{rs} = \int \phi_r^2(1)\phi_s^2(2)(1/r_{12})d\mathbf{v}_1d\mathbf{v}_2$ . Only one- and two-center type integrals are considered. The tables of Kotani *et al.*,<sup>5</sup> Roothaan,<sup>6</sup> and Rudenberg<sup>7</sup> are used. The resonance integral  $\beta_{rs} = \int \phi_r|\phi_s|d\mathbf{v}$  is neglected except first neighbors. The  $\beta$  for C—C neighbors has been given the value suggested by Pariser and Parr<sup>8</sup> for benzene, namely,  $\beta_{C-C} = -2.39$  ev, and the ones for Fe—C neighbors are assumed to be proportional to the overlap integrals.<sup>9</sup> Two structures are considered separately.

(a) When one ring is a reflection of the other by the horizontal plane: the direction combining two centers of ring is written as the  $x$ -axis, and the one through the position 5' of C is written as the  $y$ -axis. Then ligand- and metal-orbitals are combined as follows:

$$(a_2'')\alpha\rho_0^+ + \beta\phi_x; (a_1')\alpha\rho_0^- + \beta\phi_x + \gamma\phi_{(x^2-y^2)}; \\ (e_1')\alpha\rho_1^- + \beta\phi_y, \alpha\rho_1^- + \beta\phi_x; (e_2')\alpha\rho_2^- + \beta\phi_{(y^2-z^2)}, \alpha\rho_2^- \\ + \beta\phi_{yz}; (e_1'')\alpha\rho_1^+ + \beta\phi_{yz}, \alpha\rho_1^+ + \beta\phi_{xz}; (e_2'')\rho_2^+, \rho_2^+.$$

The MO energies obtained are  $-15.45$  ev ( $a_2''$ ),  $-5.88$  ev ( $a_2''^*$ ),  $-16.80$  ev ( $a_1'$ ),  $-8.57$  ev ( $a_1'^*$ ),  $-7.07$  ev ( $a_1''^*$ ),  $-7.68$  ev ( $e_1'$ ),  $-3.99$  ev ( $e_1'^*$ ),  $-7.87$  ev ( $e_2'$ ),  $-3.64$  ev ( $e_2'^*$ ),  $-8.90$  ev ( $e_1''$ ),  $-5.28$  ev ( $e_1''^*$ ), and  $-3.68$  ev ( $e_2''$ ).

(b) When one ring is an inversion of the other by the center of molecule: for symmetries  $a_1'$ ,  $a_2''$ ,  $e_2''$  MO's are the same as (a); for symmetries  $e_1'$ ,  $e_2'$ ,  $e_1''$  there are interactions between, for example,  $\rho_1^-$ ,  $\phi_y$  and  $\rho_1^-$ ,  $\phi_x$ , but when from doubly degenerated orbitals  $\rho_1''$ ,  $\rho_1''$  we make a new set of orbitals  $\bar{\rho}_1''$ ,  $\bar{\rho}_1''$ , it proves that  $\bar{\rho}_1''$  combines only with  $\phi_y$  and  $\bar{\rho}_1''$  only with  $\phi_x$ . The results are the same as (a).

The ground state has the closed shell configuration  $A:(a_1')^2(a_2'')^2(e_1'')^4(a_1'^*)^2(e_2'')^4(e_1')^4$ , and the Fe—C bonding is 33% ionic, 67% homopolar on the average.

Next, only singly excited states are considered for transitions. As the dipole moments of the molecule  $M_x$ ,  $M_y$ ,  $M_z$  belong to symmetries  $A_2''$ ,  $E_1'$ ,  $E_1'$ , respectively, there exist 10 allowed transitions from the ground state. Without CI the transition energies to low excitation levels are 0.9 ev, 3.8 ev ( $A_1' \rightarrow E_1'$ ); 2.5 ev, 3.7 ev ( $A_1' \rightarrow A_2''$ ).

<sup>1</sup> E. A. Seibold and L. E. Sutton, *J. Chem. Phys.* **23**, 1967 (1955).

<sup>2</sup> Wilkinson, Rosenblum, Whiting, and Woodward, *J. Am. Chem. Soc.* **74**, 1215 (1952).

<sup>3</sup> C. C. J. Roothaan, *Revs. Modern Phys.* **23**, 69 (1951).

<sup>4</sup> J. C. Slater, *Phys. Rev.* **36**, 57 (1930).

<sup>5</sup> Kotani, Amemiya, Ishiguro, and Kimura, *Table of Molecular Integrals* (Maruzen Company, Ltd., 1955).

<sup>6</sup> C. C. J. Roothaan, *J. Chem. Phys.* **19**, 1445 (1951).

<sup>7</sup> K. Rudenberg, *J. Chem. Phys.* **19**, 1459 (1951).

<sup>8</sup> R. Pariser and R. G. Parr, *J. Chem. Phys.* **21**, 767 (1953).

<sup>9</sup> Mulliken, Rieke, Orloff, and Orloff, *J. Chem. Phys.* **17**, 1248 (1949).

## Simultaneous Light-Absorption and Emission Measurements behind a Shock Wave\*

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(Received April 4, 1956)

IN connection with current extensive studies on the rate of carbon formation behind weak shocks in acetylene, it proved to be desirable to obtain simultaneous light-absorption and emission data. The absorption experiments are complicated because of intense emitted radiation associated with chemical reaction behind the shock front. One method for separating the emitted component from the transmitted light involves the use of carefully matched photocells and subtracting the emitted radiation from the sum of the transmitted and emitted radiation.<sup>1</sup> Another method involves the use of chopped light for the absorption measurements. However, the chopping rate places an upper limit on the rates of reaction that can be studied. A Kerr cell<sup>2</sup> using

nitrobenzene can be used to modulate the light at frequencies greater than 10 megacycles without appreciable attenuation and is therefore suitable for the study of reaction rates behind weak shocks.

The use of a Kerr cell<sup>3</sup> made it possible to study simultaneously emission and absorption during the decomposition of acetylene behind weak shocks. The light source was a General Electric Type 524 xenon lamp, with a peak intensity of 50 million lumens when pulsed for 1 millisecond. This lamp was operated so that its peak radiation lasted about 400 microseconds. The lamp was fired by discharging a capacitor through a thyratron tube which was suitably delayed so that the peak intensity of the xenon source occurred during the time that the shock passed the observation station in the shock tube. The light from the xenon source passed through the Kerr cell and then through the shock tube. Both the emitted light and the transmitted modulated light (with or without the use of a suitable monochromator) may be detected on a single photomultiplier tube whose output is then displayed on an oscilloscope. The ac component of the phototube output represents the transmitted light, the dc component corresponds directly to the emitted light.<sup>4</sup>

Another possible use of the Kerr cell involves the use of a Kerr-cell modulated prism as beam deviator followed by a monochromator.<sup>5</sup> This combination may be used as a high-speed scanning monochromator with time resolution sufficient for studies behind weak shocks.

It is felt that the successful development of new high-speed recording and scanning devices will facilitate full utilization of the potentials of the shock tube for quantitative high-temperature gas dynamic investigations.

\* Work supported by the Office of Naval Research under Contract Nonr-220(03), NR 015 401 and by the U. S. Air Force Office for Scientific Research under Contract AF 18(603)-2. The author is indebted to Dr. S. S. Penner for helpful discussions.

<sup>1</sup> Experiments of this type have been carried out by Mr. W. Hooker of our staff while he was associated with the General Electric Company.

<sup>2</sup> The use of the Kerr cell was suggested by Dr. N. Davidson.

<sup>3</sup> The author is indebted to Dr. A. Ellis for the use of his Kerr cell.

<sup>4</sup> This arrangement permits several obvious extensions. For example, the emitted radiation in several distinct wavelength regions can be chopped at different frequencies and recorded simultaneously on a single photoelectric receiver.

<sup>5</sup> This method of approach was suggested by Dr. S. S. Penner and has been studied by Dr. V. Vali of the Lockheed Aircraft Company.

## Comparison of Infrared and Cryoscopic Studies of Solutions of Pyrrole in Nonpolar Solvents. Formation of Polymers\*

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EXAMINATION of the infrared spectra of pyrrole in medium concentrations in carbon tetrachloride<sup>1</sup> enables one to distinguish two bands attributed to the stretching vibration of the NH group. Of the two, the sharper, higher frequency band alone persists in very dilute solutions. The broader, lower frequency band, on the contrary, is the only band of the pair which remains in the spectrum of pure pyrrole. These results, which have also been obtained by Mirone<sup>2,3</sup> and Tuomikoski,<sup>4-6</sup> have been confirmed by Raman spectroscopy.<sup>7</sup>

A number of different hypotheses have been proposed to account for this association. Josien *et al.*,<sup>1,8,9</sup> and Mirone<sup>2,3</sup> independently attributed the higher frequency band to the NH vibration of "free" molecules, and the lower frequency band to NH vibrations of pyrrole molecules associated by means of hydrogen bonds of N—H...N type. Tuomikoski<sup>4,6</sup> questioned the presence of NH...N hydrogen bonding, stating that the graph points for pyrrole "fall into the class of nonhydrogen-bonded liquids"<sup>6</sup> in both Pauling's<sup>10</sup> and Kumler's<sup>11</sup> studies of dipole moment as a