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Structure of CH₂

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Comment on "Note on a Paper by Rothstein"

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IT was brought to the attention of the author, too late to make reference to it, that Kunkel¹ had solved the monomolecular source-bimolecular sink problem in terms of known functions by the same method as Weiss, his Eq. (20) being the same as the final expression of Weiss. However, this function involves five distinct transcendental functions, of which the simplest (the exponential) appears in the argument of the other four as well as multiplying an algebraic expression involving them. It is very awkward for calculations with experimental data; this can no longer be said for $\text{deb}(x)$.

More recently, Dr. L. Gold has brought the earlier work of Chien² to the author's attention, in which essentially the same development as Kunkel's is presented.

¹ W. B. Kunkel, *Phys. Rev.* **84**, 218 (1951).

² J. Y. Chien, *J. Am. Chem. Soc.* **70**, 2256 (1948).

Structure of CH_2^\dagger

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RECENTLY Gallup¹ has calculated that CH_2 exists in a triplet ground state, with a bond angle of 160° , in contrast to the theoretical conclusions of Lennard-Jones² and the experimental evidence from the reactions of diazomethane with olefins.³ However, it must be pointed out that the calculation in reference 1 is not based on the lowest valence state available to a carbon atom which is only participating in two single bonds. There is a divalent valence state based on the configuration $(s^2)p^2$ as opposed to the tetravalent valence state implicitly used by Gallup which is 180° kcal higher. The bond angle of this state will be 90° without configuration interaction and a few degrees greater when configuration interaction is included due to a small amount of s character in the bonds. The next lowest state will be the triplet which Gallup claims is the ground state. Without configuration interaction it would have a bond angle of 180° , which would be somewhat smaller in the higher approximations, as Gallup actually found. The same is true of Gallup's singlet state, which however may not be the third highest level due to the possibility of a low-lying triplet from a higher configuration.

In the case of diphenylmethylen, the triplet state may be closer to the ground state than in methylene itself because of the possibility of extra conjugation. If the molecule is approximately linear, with the benzene rings in planes at right angles to each other, each could conjugate independently with a p electron on the central carbon atom (the σ bonds from the latter being approximately sp) thus lowering the energy by approximately twice the excess resonance energy of a benzyl radical over benzene itself, i.e., about 45 kcal. However, this state would still be ~ 140 kcal above the ground state, and it seems that this must always be the case whatever the substituents.

The author wishes to thank Dr. L. Pauling for discussion and advice during the course of this work, and the California Institute of Technology, Pasadena, for the award of an A. A. Noyes Research Fellowship in chemistry.

† Contribution No. 2280 from the California Institute of Technology, Pasadena, California.

¹ G. A. Gallup, *J. Chem. Phys.* **26**, 716 (1957).

² J. E. Lennard-Jones, *Trans. Faraday Soc.* **30**, 70 (1934).

³ Skell and Woodworth, *J. Am. Chem. Soc.* **78**, 4496 (1956).

Structure of CH_2

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GRAY¹ has criticized the calculation of the ground state multiplicity of the CH_2 fragment by the author.² In answer, I would like to make two comments.

1. Regardless of the energies of ionization of a carbon atom, CH_2 may be considered as a system composed of two protons, a carbon kernel, and four electrons. The proper amount of configuration interaction should arise naturally and depend on relative energies of orbitals and overlap values. It appears that there is too much configuration interaction in the calculation in reference 2 since the equilibrium angle arrived at is 160° instead of 140° as obtained by Herzberg. (See reference 3 of reference 2.) Nevertheless, the measured angle of 140° seems to the author to be considerably greater than a few degrees greater than 90° and to indicate a considerable amount of configuration interaction.

2. Noyes³ has obtained data on photocatalyzed gas reactions of hydrocarbons that give indications of the presence of CH_2 fragments as intermediates. There is also a suggestion that these may be in triplet states. This certainly cannot be said to have been proved, however.

¹ B. F. Gray, *J. Chem. Phys.* **28**, 1252 (1958), preceding letter.

² G. A. Gallup, *J. Chem. Phys.* **26**, 716 (1957).

³ W. A. Noyes, Jr. (private communication).