Richard Eisenberg[15]
Department of Chemistry, Columbia University
New York, New York 10027

James A. Ibers
Department of Chemistry, Brookhaven National Laboratory
Upton, New York 11973

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Energy Level of the First Excited Singlet State of 1,3-Butadiene

Sir:

It is well known that the intense absorption in the ultraviolet spectrum of 1,3-butadiene, which has a maximum at 2100 Å., corresponds to a $\pi \rightarrow \pi^*$ transition from the ground singlet to an upper singlet state. Although this absorption has been studied extensively from both an experimental and a theoretical point of view,[1,2] it has not been possible to identify the 0 → 0 band as the absorption shows very little detailed structure, and fluorescent emission has never been observed from this state. It has been assumed that the 0 → 0 band lies not far from the point where the absorption falls off in intensity, which is approximately 2300 Å.[3] The exact position of the singlet excited state is a matter of importance for photochemical purposes. Thus, it is believed that a considerable energy gap separates the first excited singlet from the lowest triplet state.[4] Obviously, the magnitude of the gap can be known only if the limits of the gap are defined. Again it is very useful to bring about the photolysis of 1,3-butadiene at 2537 Å. It is necessary to know the reactive state that is produced at this wave length. Since data on the energy levels of the excited singlet states of none of the simple 1,3-dienes are available, the discussion here is of a fairly general nature.

The intensity of the absorption spectrum of 1,3-butadiene decreases from its maximum value of 24,000 cm.[2] mole^{-1} at 2100 Å. to 280 at 2300 Å., but at 2500 Å. it is still 4.4.[5] It is the purpose of this communication to point out that the excited state that is generated on the absorption of 2537-Å. radiation is probably an upper singlet and that the 0 → 0 band for this state must lie at a wave length considerably larger than this.

We have now observed that photolysis of 1,3-butadiene in hydrocarbon solution at 2537 Å. gives rise *exclusively* to cyclobutene and bicyclo[1.1.0]butane in dilute solution. The ratio of cyclobutene to bicyclobutane is independent of temperature from 0 to 50° and changes with the nature of the solvent (ether, 7; isooctane, 14).[6] These valence tautomerization reactions cannot be ground-state reactions since in the ground state the thermodynamic equilibria are in favor of 1,3-butadiene. The choice is then between the excited singlet and the lowest triplet states. Since photosensitization of 1,3-butadiene by a variety of sensitizers in their triplet states does not give either of these valence tautomers,[7] it seems unlikely that the triplet state is the reactant during photolysis at 2537 Å. This reduces the choice to the upper singlet state alone.

We have also observed that the dimerization of 1,3-butadiene at 2537 Å. in the absence of any sensitizer differs markedly from the dimerization initiated by a triplet sensitizer[7] and from the thermal process. In the first place, even at an optimum concentration, photodimerization accounts for less than 10% of the butadiene that is consumed, whereas in the triplet-sensitized reaction, the yield of dimers is nearly 75%. [At high concentrations, polymeric materials are formed predominantly, but these do not seem to be related to polymers formed by free radical (thermal) polymerization.] In the second place, the most important dimer (50%) that is observed is neither 1,2-divinylcyclobutane (I) (although this accounts for 30% of the yield) nor 4-vinylcyclohexene (II) (which is

I
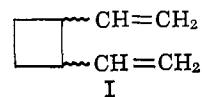
negligible, if at all present), but a compound which

II
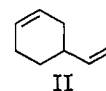
on analysis fit the formula C_8H_{12} (*Anal.* Calcd. for C_8H_{12}: C, 88.82; H, 11.17. Found: C, 89.02; H, 11.17) and showed the presence of a vinyl group (1640, 994, and 915 cm.$^{-1}$) and a cyclopropyl group (1026 cm.$^{-1}$) in its infrared spectrum. The n.m.r. spectrum showed the presence of three vinyl protons, four cyclopropyl protons, one allylic proton, and four other protons centered at τ 8.5. This would correspond to the structure 2-vinylbicyclo[3.1.0]hexane (III).[8]

III
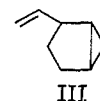
About 8% of the products was 1,5-cyclooctadiene, which has been reported in the triplet-sensitized reaction as well as in the thermal dimerization. A fourth dimer, which amounted to about 10% of the total, was not identified.

It is possible that on absorption of a photon at 2537 Å. butadiene undergoes a transition from a ground singlet to a high vibrational level of the second triplet observed by Evans.[9] However, in this state bimolecular processes, such as those necessary to lead to dimerization, would compete unfavorably with vibrational deactivation and electronic quenching to the

(1) A. Smakula, *Angew. Chem.*, **47**, 657 (1934); G. Scheibe and H. Grieneisen, *Z. physik. Chem.*, **B25**, 54 (1934).
(2) N. L. Allinger and J. C. Tai, *J. Am. Chem. Soc.*, **87**, 2081 (1965), and references therein.
(3) The specific instance of 1,3-pentadiene is discussed by G. S. Hammond, N. J. Turro, and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1144 (1962).
(4) I. Haller and R. Srinivasan, *J. Chem. Phys.*, **40**, 1992 (1964).
(5) American Petroleum Institute Research Project 44, Ultraviolet Spectral Data, Serial No. 65.
(6) Details of these studies will be published elsewhere.
(7) G. S. Hammond, N. J. Turro, and A. Fisher, *J. Am. Chem. Soc.*, **83**, 4674 (1961).
(8) The alternative structure of 3-vinylbicyclo[3.1.0]hexane is not rigorously excluded.
(9) D. F. Evans, *J. Chem. Soc.*, 1735 (1960).

first triplet state. The best hypothesis appears to be that, at 2537 Å., 1,3-butadiene is excited to the upper singlet state. It follows that the 0–0 level must lie at even longer wave lengths. The simplest conjugated diene from which fluorescence has been observed is ergosterol.[10] In this case, the fluorescent spectrum exactly reproduces the absorption spectrum but is shifted by nearly 1000 Å. to the red. A similar situation obtains in lumisterol, another cyclic 1,3-diene.[10] In both molecules, there is no detectable absorption which corresponds to the 0–0 band from the ground singlet to the upper singlet. It seems possible that in 1,3-butadiene the 0–0 band may lie at a wave length as low in energy as 90 kcal./mole (~3200 Å.). Since the lowest triplet lies at 60 kcal./mole,[9] the gap that separates these two levels is in no sense "large." [The upper singlet–lowest triplet separation in benzene is 25.5 kcal./mole.[11]]

(10) E. Havinga, R. J. De Kock, and M. P. Rappoldt, *Tetrahedron*, 11, 276 (1960).
(11) H. Ishikawa and W. A. Noyes, Jr., *J. Chem. Phys.*, 37, 583 (1962).

R. Srinivasan, F. I. Sonntag
IBM Watson Research Center
Yorktown Heights, New York

On the Equations Used to Analyze Isotropic Nuclear Magnetic Resonance Shift Data for Systems Involving a Rapid Equilibrium

Sir:

The equation

$$\frac{\Delta H_i}{H} = \frac{\Delta f_i}{f} = -\frac{A_i}{2S}\frac{\gamma_e}{\gamma_H}\frac{g\beta S(S+1)}{kT}[3 + \exp(\Delta G/RT)]^{-1}$$

(1)

has been used many times[1-11] to analyze the results of isotropic n.m.r. shifts of nickel chelates in solution where there is a square-planar (singlet) ⇌ tetrahedral (triplet) equilibrium in solution. In this equation ΔH_i and Δf_i are the isotropic shifts from the diamagnetic position of the resonance magnetic field and frequency, respectively, of a given nucleus. A_i is the isotropic hyperfine coupling constant for the ith proton, γ_e and γ_H are the magnetogyric ratios of the electron and proton, respectively, g is the spectroscopic splitting factor for the paramagnetic species, and ΔG is the free energy change for the above-mentioned equilibrium. The other symbols have their usual significance.

(1) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *J. Chem. Phys.*, 37, 347 (1962).
(2) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *Mol. Phys.*, 5, 497 (1962).
(3) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *Discussions Faraday Soc.*, 34, 77 (1962).
(4) W. D. Phillips and R. E. Benson, *J. Chem. Phys.*, 33, 607 (1960).
(5) D. R. Eaton, A. D. Josey, R. E. Benson, W. D. Phillips, and T. L. Cairns, *J. Am. Chem. Soc.*, 84, 4100 (1962).
(6) D. R. Eaton, W. D. Phillips, and D. J. Caldwell, *ibid.*, 85, 397 (1963).
(7) D. R. Eaton, A. D. Josey, and W. A. Sheppard, *ibid.*, 85, 2689 (1963).
(8) R. H. Holm, A. Chakravorty, and G. O. Dudek, *ibid.*, 86, 379 (1964).
(9) A. Chakravorty and R. H. Holm, *ibid.*, 86, 3999 (1964).
(10) A. Chakravorty and R. H. Holm, *Inorg. Chem.*, 3, 1010 (1964).
(11) G. W. Everett, Jr., and R. H. Holm, *J. Am. Chem. Soc.*, 87, 2117 (1965).

As noted in footnote 31a of ref. 8, the $2S$ in the denominator of eq. 1 is involved with the relationship between the unpaired electron spin density and the A_i values. This point will not concern us further here. Equation 1 reduces (when $\Delta G \to -\infty$) correctly to eq. 2[12] which is applicable to fully paramagnetic systems in which the isotropic shifts obey the Curie law

$$\frac{\Delta H_i}{H} = -\frac{A_i}{2S}\frac{\gamma_e}{\gamma_H}\frac{g\beta S(S+1)}{3kT}$$

(2)

The observed isotropic shifts for a system in rapid equilibrium will be the isotropic shifts for the diamagnetic species (zero by definition) and paramagnetic species, weighted by their mole fractions in solution. If we call the mole fraction of triplet molecules N_T, then the isotropic shifts are given by

$$\frac{\Delta H_i}{H} = -\frac{A_i}{2S}\frac{\gamma_e}{\gamma_H}\frac{g\beta S(S+1)}{3kT}N_T$$

(3)

It is easily shown that the equilibrium constant K for the singlet–triplet equilibrium is $K = [(1/N_T) - 1]^{-1}$, and also since $\Delta G = -RT \ln K$ we have: $\Delta G = RT \ln [(1/N_T) - 1]$.[13] We get immediately that $N_T = [\exp(\Delta G/RT) + 1]^{-1}$, so that the correct equation for isotropic shifts, when an equilibrium is involved, is

$$\frac{\Delta H_i}{H} = -\frac{A_i}{2S}\frac{\gamma_e}{\gamma_H}\frac{g\beta S(S+1)}{3kT}[\exp(\Delta G/RT) + 1]^{-1}$$

(4)

Furthermore, the equation given[6,8] for the molar magnetic susceptibility of these systems

$$\chi_M = \frac{2g^2N\beta^2}{3kT}[1 + 1/3 \exp(\Delta G/RT)]^{-1}$$

(5)

and the corollary equation[6,8,10,11] for the free energy change in terms of the measured effective magnetic moment values, μ_{eff}

$$\Delta G = RT \ln 3 \left[\frac{\mu_\infty^2}{\mu_{eff}^2} - 1\right]$$

(6)

are incorrect and should in fact be, respectively

$$\chi_M = \frac{2g^2N\beta^2}{3kT}[\exp(\Delta G/RT) + 1]^{-1}$$

(7)

and

$$\Delta G = RT \ln \left[\frac{\mu_\infty^2}{\mu_{eff}^2} - 1\right]$$

(8)

The error no doubt arose from a misapplication of the formula[14] for the magnetic susceptibility of a substance which has a singlet ground state and a thermally accessible triplet state separated from the ground state by an energy J. The molar susceptibility of such a system is correctly given by

$$\chi_M = \frac{2g^2N\beta^2}{3kT}[1 + 1/3 \exp(J/kT)]^{-1}$$

(9)

However, it is not permissible to replace the energy quantity J by a free energy ΔG, while retaining the degeneracy factor $1/3$. The degeneracy factor is embodied

(12) H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, 29, 1361 (1958).
(13) The analogous eq. 5 of ref. 6 is in error.
(14) B. N. Figgis and R. L. Martin, *J. Chem. Soc.*, 3837 (1956).