

2,4,6-trinitrotoluene (TNT), *sym*-trinitrobenzene (TNB) and 2,4,7-trinitro-9-fluorenone (TNF). The spectral effects are similar to those observed by Gouterman³ for zinc tetraphenylporphyrin and are consistent with the formation of 1:1 complexes of the (predominantly) charge-transfer type. Neglecting solvent competition, the equilibrium constants, K_e , were found to be approximately 2.3, 10 and 345 l./mole at 25° for TNT, TNB and TNF, respectively, in acetone solution.⁴

A detailed study of the quenching of fluorescence of zinc phthalocyanine by a series of aryl nitro-compounds (A) has established the following: (a) the emission spectra of the quenched and unquenched solutions are identical; (b) the extent of quenching is greater than can be accounted for by ground state complex formation alone; (c) the ratio of fluorescence yields (γ^0/γ) in the absence and presence of A varies linearly with the quencher concentration [A] for weaker quenchers; whereas, (d) for the strongest quenchers, the data are closely fitted by the expression

$$\gamma^0/\gamma = \{1 + k[A]\} \{1 + K_e[A]\} \quad (1)$$

where k is a constant and K_e is the ground state equilibrium constant determined independently from the absorption spectra. The sequence of values of the constant k appears to be that of the electron affinities of the quenchers. In Table I, k is correlated with the available positions of the charge transfer absorption bands of the corresponding hexamethylbenzene complexes.⁵

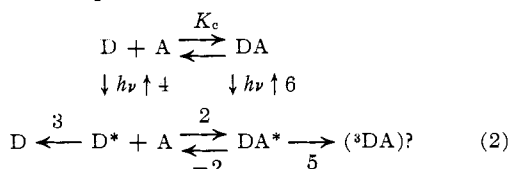
TABLE I

VALUE OF k IN ACETONE AT 25°

The last column gives the position of the corresponding hexamethylbenzene charge transfer complex absorption band in cyclohexane.

Quencher (acceptor)	Range of quencher concentrations, M	k , l. mole ⁻¹	λ (H.M.B. complex), $m\mu$
<i>p</i> -Nitrotoluene	0.05-0.40	1.6	...
Nitrobenzene	.05-0.40	3.0	...
2,4-Dinitrotoluene	.005-0.035	42	323
1,3-Dinitrobenzene	.005-0.035	47	343
2,4,6-Trinitrotoluene	.001-0.018	52	376
1,3,5-Trinitrobenzene	.001-0.018	75	387

The simplest interpretation of these observations is that in addition to forming ground state complexes, zinc phthalocyanine readily functions as an electron donor in the excited state with the result that the efficiencies of both the static and diffusional parts of the quenching mechanism are determined by the acceptor strengths of the quenchers. Thus we have



in which D, D*, DA and DA* represent ground state and excited fluor and complex, respectively. With $k = k_2/(k_3 + k_4)$ this gives eq. 1, provided that $k_5 \gg (k_6 + k_{-2})$ and is consistent with (a), (b) and (c). The absorption spectra show that D* and DA* have

(3) M. Gouterman, *J. Chem. Phys.*, **37**, 2266 (1962).

(4) The use of the unfavorable solvent acetone is due to the insolubility of zinc phthalocyanine in inert solvents. The surprisingly high K_e for the TNF complex does not rest on absorption data alone. Thus, the fluorescence of zinc phthalocyanine is quenched by TNF at a rate some fivefold greater than would be calculated on the basis of a diffusion controlled reaction and a reasonable estimate of the fluorescence lifetime.

(5) G. Briegleb, "Electronen-Donator-Acceptor-Komplexe," Springer-Verlag, West Berlin, 1961.

similar radiative lifetimes so that the absence of kinetic or spectroscopic evidence for DA* emission implies an extremely fast radiationless deactivation of DA*, probably by intersystem crossing as observed for the TNB complex of anthracene.⁶ This suggestion cannot be tested readily since the phosphorescence of phthalocyanines occurs in the infrared.⁷ Although we were able to populate the triplet state of zinc phthalocyanine by a flash photolytic method, the triplet yields could not be measured in the presence of the acceptors which were found to catalyze the triplet decay.

Picric acid was found to be exceptional in that its extremely strong complex with zinc phthalocyanine in acetone exhibits a new absorption band at 705 $m\mu$ and a new emission band at 714 $m\mu$. These are not typical charge transfer transitions and probably represent a perturbation of the pigment molecule by formation of a strong hydrogen bond. The two moieties in this complex presumably are not coplanar with the result that process 5 is inhibited, the radiative step 6 is observed and the over-all effect is one of fluorescence enhancement. This type of behavior has been observed for numerous phthalocyanines and porphyrins and will be described in detail elsewhere.

(6) M. Kleinerman, L. Azarraga and S. P. McGlynn, in "Luminescence of Organic and Inorganic Systems," John Wiley and Sons, Inc., New York, N. Y., 1962.

(7) R. S. Becker and M. Kasha, *J. Am. Chem. Soc.*, **77**, 3669 (1955).

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Carbon Orbital Hybridizations and Acidity of the Bicyclobutane System^{1,2}

Sir:

As part of a program designed to correlate chemical reactivity with hybridizations of carbon atomic orbitals in small ring compounds,³ we have examined the ¹³C-H nuclear spin-spin coupling of tricyclo[4.1.0.0.2.7]heptane (I). The readily available tricyclic hydrocarbon I, recently reported by Moore and collaborators,⁴ is thought to be a valid model for the bicyclobutane system, because the trimethylene bridge should be flexible enough not to introduce further strain into the system.

The following coupling constants were found for the carbon-13 satellites in the proton magnetic resonance spectrum of I

¹³C₁-H, 200 ± 2; ¹³C₂-H, 146 ± 2; ¹³C₃-H, ¹³C₄-H, 125 ± 2 c.p.s.

(average of two indistinguishable coupling constants).^{5,6}

Applying the well substantiated correlation of coupling constants with carbon atomic orbital hybridizations,⁷ one arrives at 40 and 29% s-character for the exocyclic orbitals of carbon atoms 1 and 2, respectively. Normal sp³ hybridization is found for the trimethylene bridge carbon atoms.

(1) Presented in part at the Carbanion Symposium of the American Chemical Society National Meeting, Los Angeles, Calif., April, 1963.

(2) This work was supported by NSF Grant G19927.

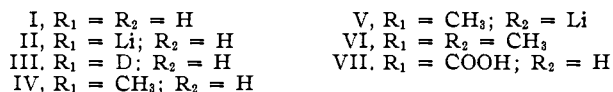
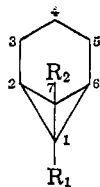
(3) Cf. G. L. Closs, *Proc. Chem. Soc.*, 152 (1962).

(4) W. R. Moore, H. R. Ward and R. F. Merritt, *J. Am. Chem. Soc.*, **83**, 2019 (1961).

(5) The carbon-13 satellite spectra were studied in natural abundance. To avoid errors in the assignment of the exceedingly weak signals, the spectra were run at 40 and 60 Mc.

(6) The vicinal proton-proton coupling constant, $J_{R_1R_2}$, was found to be 11.5 ± 0.5 c.p.s.

(7) N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 768, 1471 (1959); J. N. Shoolery, *ibid.*, **31**, 1427 (1959); C. Juan and H. S. Gutowsky, *ibid.*, **37**, 2198 (1962).



The remarkably high degree of s-character of the C_1 -H bond led us to expect unusual acidity of the hydrocarbon. This prediction was verified when it was observed that I reacted with *n*-butyllithium in ether to form quantitatively the bicyclobutyl lithium II,⁸ from which I could be regenerated on hydrolysis, and which was converted to III on treatment with deuterium oxide. The n.m.r. spectrum of III establishes the position of the deuterium atom, since the triplet at 8.55 τ in the spectrum of I, attributed to the protons at positions 1 and 7, is replaced in the spectrum of III by an unresolved multiplet of one half the intensity.⁹ Reaction of II with methyl iodide gave IV (b.p. 66° (100 mm.), n_D^{20} 1.4580; n.m.r. (CCl₄) 7.86 (m), 8.48 (s), 8.75 (m), 9.00 (t) τ , relative areas 2:3:6:1), while carbonylation yielded VII (m.p. 84.5–86.0°; n.m.r. (CCl₄) -1.90 (s), 6.89 (m), 7.75 (t), 8.55 (m) τ , relative areas 1:2:1:60; ultraviolet (pentene) end abs. 220 $m\mu$, ϵ 7,700; pK_a 4.6). The carbon-13 hydrogen coupling constants at positions 2 and 7 in IV are identical within experimental error with those measured for I. Again, the high degree of s-character of the C_7 -H bond in IV is reflected in the reaction with *n*-butyllithium yielding V. Treatment of V with methyl iodide resulted in the formation of VI (b.p. 72° (20 mm.); n_D^{20} 1.4529; n.m.r. 8.20 (m), 8.73, (s), 8.76 (m) τ , relative areas of the 8.20 signal to the sum of the 8.73 and 8.76 peaks 1:6.¹⁰

Further evidence for the acidity of the bicyclobutane system was obtained from deuterium-hydrogen exchange studies on III carried out in *t*-butyl alcohol with potassium *t*-butoxide as catalyst. Conversion of III to I follows first-order kinetics (k_1 at 99.5° and 0.61 mole/l. potassium *t*-butoxide = 2×10^{-7} sec.⁻¹).

The results reported here are in qualitative agreement with the generally accepted theory of bonding in small ring compounds¹¹ which predicts unusually high degree of s-character for the exocyclic carbon orbitals. Comparison of the data with those obtained for 1,3,3-trimethylcyclopropene (¹³C₁-H 220 c.p.s., corresponding to 44% s-character³; deuterium-hydrogen exchange approximately 10⁴ times faster than III) indicates a certain qualitative analogy between the two ring systems. However, it remains to be established whether the considerably larger exchange rate of the cyclopropene is caused mainly by the somewhat higher s-character of the =C-H bond, or whether the induc-

(8) At 25° and concentrations of 1 mole/l. of each reactant, the half-reaction point is reached after approximately 3 hr.

(9) The n.m.r. spectrum of I reported by Moore¹ for the neat compound consists of three signals, 7.58 (m) for protons at carbon 2 and 6, 8.33 (t) for protons at 1 and 7 and 8.55 (m) τ for the methylene protons. These values change in carbon tetrachloride to 7.72, 8.55 and 8.71 τ . The assignments of the resonances made by Moore were further supported by spin decoupling experiments carried out in our Laboratory. It was shown that the protons giving the signal at 7.72 τ are coupled with both the methylene protons and the protons whose signal appears at 8.55 τ . The latter are only coupled with the 7.72 resonance.

(10) Compounds I, III, IV and VI were purified by vapor phase chromatography. Satisfactory analyses were obtained for all new compounds.

(11) C. A. Coulson and W. E. Moffitt, *J. Chem. Phys.*, **15**, 151 (1947); A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).

tive effect of the double bond is a strongly contributing factor.

(12) Alfred P. Sloan Foundation Fellow.

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The Temperature-Independent Factor of the Kinetic Isotope Effect¹

Sir:

In eq. 1 for the kinetic isotope effect in terms of vibration frequencies of reactants and activated com-

$$\frac{k}{k'} = \frac{\nu_L^*}{\nu_L'^*} \prod_i^{3n^*-7} \frac{\nu_i^*}{\nu_i'^*} e^{-\Delta u_i^*/2} \frac{(1 - e^{-u_i^*})}{(1 - e^{-u_i'^*})} \prod_j^{3n-6} \frac{\nu_j'}{\nu_j} e^{\Delta u_j/2} \frac{(1 - e^{-u_j})}{(1 - e^{-u_j'})}$$

plex, the factor $\nu_L^*/\nu_L'^*$ has been widely designated^{2,3} as "the temperature-independent factor." Bigeleisen and Wolfsberg² derived expression 2 for this factor for a linear triatomic activated complex with masses m_1 ,

$$\frac{\nu_L^*}{\nu_L'^*} = \left[\frac{(\mu_{23} + p\mu_{12} + 2p^{1/2}\mu_2)}{(\mu'_{23} + p\mu'_{12} + 2p^{1/2}\mu'_2)} \right]^{1/2} \quad (2)$$

m_2 and m_3 and internuclear distances r_1 and r_2 , where $\mu_{12} = m_1^{-1} + m_2^{-1}$, $\mu_{23} = m_2^{-1} + m_3^{-1}$, $\mu_2 = m_2^{-1}$, and $p^{1/2}$, which equals β/α , "determines the relative amount of bond formation to bond rupture"² in the reaction coordinate $x_L = \alpha r_2 - \beta r_1$. Yankwich and Ikeda⁴ extended the calculation to other transition-state geometries and to $n = 4$.

The actual temperature-independent factor obtained by extrapolation is, however, not usually $\nu_L^*/\nu_L'^*$ at all, but depends on the experimental conditions and the extrapolation method. If all real vibration frequencies of both reactants and transition state are greater than about $6kT/h$, eq. 1 becomes

$$k/k' = \tau_* \tau_r^{-1} e^{-\left[\sum_i^{3n^*-7} \Delta u_i^*/2 - \sum_j^{3n-6} \Delta u_j/2 \right]} \quad (3)$$

$$\tau \equiv \prod_i^{3n-6} \nu_i/\nu_i' \quad (4)$$

where the symbols * and r refer to transition state and reactants, respectively. Under these conditions (high frequencies or low temperature), $\ln(k/k')$ vs. $1/T$ is linear with infinite-temperature intercept $\ln \tau_* \tau_r^{-1}$. For the linear triatomic activated complex the contribution to τ_* from the two linear vibrations (one of which is $\nu_L^*/\nu_L'^*$) can be calculated, most easily by the FG-matrix method of Wilson, Decius and Cross,⁵ to be

$$\nu_1 \nu_2 / \nu_1' \nu_2' = \{(\mu_{12} \mu_{33} - \mu_2^2) / (\mu'_{12} \mu'_{33} - \mu_2'^2)\}^{1/2} \quad (5)$$

Note that this is entirely independent of any structural features of the transition state other than the masses and their mutual ordering. Evidently the variations with transition-state structure which are predicted for the imaginary-frequency ratio by eq. 2 are precisely cancelled by converse variations in the other linear-fre-

(1) Supported in part by the Atomic Energy Commission under Contract No. AT(30-1)-905.

(2) J. Bigeleisen and M. Wolfsberg, *J. Chem. Phys.*, **21**, 1972 (1953); **22**, 1264 (1954); J. Bigeleisen and M. Wolfsberg, *Advan. Chem. Phys.*, **1**, 15 (1958).

(3) For example, see L. Melander, "Isotope Effects on Reaction Rates," Ronald Press Co., New York, N. Y., 1960, p. 38.

(4) P. E. Yankwich and R. M. Ikeda, *J. Am. Chem. Soc.*, **81**, 1532 (1959).

(5) E. B. Wilson, Jr., J. C. Decius and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., New York, N. Y., 1955, p. 183. From their eq. 3 it follows that $\tau = |\mathbf{G}^{1/2}/|\mathbf{G}'|^{1/2}$. The \mathbf{F} determinants cancel because the force constants are the same for isotopic molecules. For this application, the \mathbf{G} matrices should be written for internal coordinates.