

Figure 1. The water-acetone dimer.

In the course of a continuing study of the carbonyl group as a proton acceptor, the water-acetone system has been investigated, and the optimized structure of the water-acetone dimer determined. The $n \rightarrow \pi^*$ transition energies in acetone, the water-acetone dimer, and a water-acetone trimer have also been calculated. These results now permit a direct comparison of theoretical and experimental values for the blue shift of the $n \rightarrow \pi^*$ band. It is the purpose of this communication to present this comparison and to interpret the results in light of previous discussions of $n \rightarrow \pi^*$ transitions in dimers.

The *ab initio* SCF calculations which have been performed employed the minimal STO-3G basis set with standard scale factors.³ The optimized geometry of acetone was first determined, and held rigid for all dimer calculations. The procedure followed for optimizing the ground state structure of the dimer is given in a previous paper.⁴ The optimized dimer, shown in Figure 1, has C_s symmetry, an intermolecular O-O distance of 2.84 Å, a linear O-H...O hydrogen bond, and an angle of 125° between the intermolecular O-O line and the C-O bond. The calculated intermolecular energy (hydrogen bond energy) is -0.00671 au. A thorough discussion of this dimer will be included in a future publication.

The vertical $n \rightarrow \pi^*$ transition energies in acetone, the water-acetone dimer, and a water-acetone trimer were calculated using the configuration interaction (CI) method. The trimer, in which the carbonyl oxygen is hydrogen bonded to two water molecules, was constructed from the optimized dimer with the restriction of C_{2v} symmetry.⁵ For monomer, dimer, and trimer, limited first-order CI functions were obtained consisting of linear combinations of 90 singly excited functions. The transition energies resulting from the CI calculations are given in Table I.

From Table I, it is evident that the calculated and experimental $n \rightarrow \pi^*$ transition energies of acetone are in very good agreement. Moreover, the experimental $n \rightarrow \pi^*$ transition energy of acetone in water is also in agreement with the calculated transition energy in the water-acetone dimer. Thus, the experimental blue shift of 0.19 eV of the $n \rightarrow \pi^*$ band of acetone in water is

(3) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).

(4) J. E. Del Bene, *J. Chem. Phys.*, **58**, 3139 (1973).

(5) Full optimization of a water-formaldehyde trimer with C_{2v} symmetry was found to lead to only a slight additional stabilization of the trimer. The $n \rightarrow \pi^*$ transition energies in the trimer constructed from the optimized dimer and in the optimized trimer were equal to within 0.01 eV.

Table I. Hydrogen Bond and $n \rightarrow \pi^*$ Transition Energies

	Hydrogen bond energy (eV)	$n \rightarrow \pi^*$ transition energy (eV)	Experimental $n \rightarrow \pi^*$ transition energy ^a (eV)
Monomer		4.48	4.49 ^b
Dimer	0.18	4.66	4.68 ^c
Trimer	0.32	4.78	

^a Experimental data are λ_{\max} values, taken from C. N. R. Rao, "Ultraviolet and Visible Spectroscopy," Plenum Press, New York, N. Y., 1967. ^b $n \rightarrow \pi^*$ energy of acetone in heptane. ^c $n \rightarrow \pi^*$ energy of acetone in water.

reproduced by the calculated blue shift of 0.18 eV in going from monomer to hydrogen-bonded dimer. On the other hand, the calculated transition energy in the trimer corresponds to a blue shift of 0.30 eV, which is greater than the experimental value. Although the calculations refer more directly to the gas phase, the above comparisons do support the existence of a water-acetone dimer, rather than the proposed trimer, in solutions of acetone in water.

Also evident in Table I is a correlation between the calculated $n \rightarrow \pi^*$ transition energies in the dimer and trimer and the hydrogen bond strengths in these species. In particular, these transition energies are approximated to within 0.02 eV, as the sum of the monomer $n \rightarrow \pi^*$ transition energy and the hydrogen bond strength in the corresponding polymer. This correlation has been observed previously in hydrogen-bonded dimers and interpreted as indicating that the blue shift reflects the additional energy required to break the hydrogen bond upon excitation to the dimer excited state.⁶

In summary, the direct comparison of theoretical and experimental $n \rightarrow \pi^*$ transition energies of acetone and acetone in water does not support the suggestion that the acetone molecule in solution is hydrogen bonded to two water molecules. Rather, the interpretation consistent with the data obtained in this study is that the acetone molecule tends to hydrogen bond to a single water molecule. The blue shift of the $n \rightarrow \pi^*$ band then reflects the additional energy required to break the hydrogen bond in the excited state of the dimer.

(6) See ref 2, and references cited therein.

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Photolysis of Cyclobutyl Aryl Ketones. Evidence for the Involvement of an Excited State Conformational Equilibrium in Their Photoconversion to Aryl Bicyclo[1.1.1]pentanols

Sir:

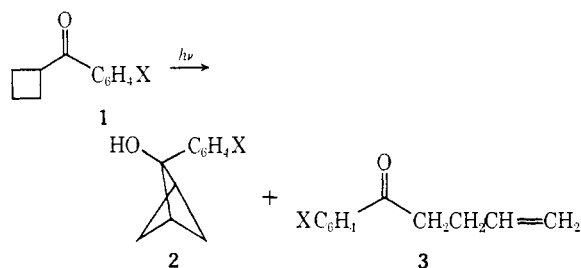
A great deal of recent research on small ring compounds has focused on bicyclo[1.1.1]pentanes.^{1,2} Among the synthetic entries³ into the ring system, the

(1) (a) A. Padwa and W. Eisenberg, *J. Amer. Chem. Soc.*, **94**, 5852 (1972); (b) *ibid.*, **92**, 5674 (1970).

(2) (a) M. D. Newton and J. M. Schulman, *J. Amer. Chem. Soc.*, **94**, 773 (1972); (b) W. Stohrer and R. Hoffman, *ibid.*, **779** (1972).

(3) (a) K. B. Wiberg and D. S. Connor, *J. Amer. Chem. Soc.*, **88**, 4437 (1966); (b) K. B. Wiberg and V. Z. Williams, *J. Org. Chem.*, **35**, 369 (1970); (c) R. Srinivason and K. H. Carrough, *J. Amer. Chem. Soc.*,

approach involving the photolysis of cyclobutyl phenyl ketone (**1a**) is the most promising. A striking feature about the reaction has been its very low quantum efficiency and slow rate of internal hydrogen abstraction.^{3e} The cyclobutane ring is puckered by about 27° and undergoes a very rapid ring inversion called pseudorotation which allows for substituted derivatives to exist in quasi-equatorial and quasi-axial conformations.⁴ Recent chemical evidence has accounted for the inefficiency of the reaction involving ketone **1a** in terms of the low concentration of its reactive quasi-axial conformer.⁵ In the present paper we wish to report a kinetic mechanism for the inefficiency which supports the chemical evidence and which further allows for the estimation of the relative concentrations of the reactive and unreactive conformers. The mechanism is based on results obtained in our laboratory on the photoconversions of the phenyl substituted cyclobutyl ketones (**1b-e**) to their



a. X = H; b, X = *p*-CH₃; c, X = *p*-F; d, X = *p*-CF₃; e, X = *o*-CF₃

corresponding bicyclic and keto olefinic isomers.⁶ There are three mechanisms that could account for the low concentration of the reactive conformer of ketone **1a** and lead to the observed inefficiency.

Mechanism 1. Quantum efficiency controlled by ground state conformational equilibrium. Recent nmr studies on substituted cyclobutanes have shown that monosubstituted cyclobutanes possessing substituents comparable^{7a} in size to the benzoyl group exist more in planar *vs.* equatorial conformations rather than in quasi-axial *vs.* quasi-equatorial ones.^{7b} Thus, of the ground state conformers expected for ketone **1a** the quasi-axial one would be the least stable thermodynamically and the least populated. The observed inefficiency and low concentration of reactive conformer might be explained, then, on the basis of the small fraction of the quasi-axial conformer of ketone **1a** existing in the ground state. For this to be the case excited ketone **1a** would be required to react according to Scheme I with $k_i \ll k_d$ and $k_r \geq k_{-i}$. Under these conditions the quantum efficiency would be represented by eq 1, where k_r is the rate constant for γ -hydrogen

$$\Phi = \alpha \left(\frac{k_r}{k_r + k_{-i}} \right) \quad (1)$$

abstraction, k_d is the rate constant for triplet deactivation,

89, 4932 (1967); (d) J. Meinwald, W. Szkrybalo, and D. R. Dimmel, *Tetrahedron Lett.*, 71 (1967); (e) A. Padwa, E. Alexander, and M. Niemczyk, *J. Amer. Chem. Soc.*, 91, 465 (1969).

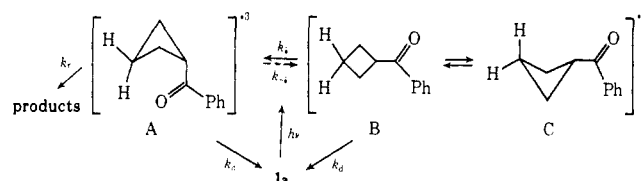
(4) J. E. Kilpatrick, K. S. Pitzer, and R. Spitzer, *J. Amer. Chem. Soc.*, 69, 2483 (1947); B. Hendrickson, *ibid.*, 83, 4537 (1961).

(5) A. Padwa and W. Eisenberg, *J. Amer. Chem. Soc.*, 94, 5859 (1972).

(6) All spectral and elemental analyses are consistent with the assigned structures and will be reported in a full paper.

(7) (a) See ref 9, p 236; (b) J. B. Lambert and J. D. Roberts, *J. Amer. Chem. Soc.*, 87, 3884 (1965).

Scheme I



tion, k_i is the rate constant for the conformation change, and α is the fraction of the reactive conformer A.

Mechanism 2. Quantum efficiency controlled by ring inversion in excited state. If only a small fraction of the ground state conformers of cyclobutyl phenyl ketone (**1a**) possess the appropriate geometry for intramolecular hydrogen abstraction, a change to the more reactive conformation may occur in the excited state. If the conformational change occurs at a rate which is slow relative to both the triplet deactivation and hydrogen abstraction processes, the reaction sequence would follow Scheme I with $k_i \leq k_d$ and $k_r > k_{-i}$. In this case the quantum efficiency would be given by eq 2.

$$\Phi = \left(\frac{k_r}{k_r + k_d} \right) \left(\frac{k_i}{k_i + k_d} \right) \quad (2)$$

According to this mechanism ring inversion would be rate limiting and would account for the low concentration of reactive conformer A and the low quantum yield. In addition the rate constant previously reported^{3e} for γ -hydrogen abstraction by ketone **1a** would be "pseudo" in nature and would equal the product of the actual rate constant for hydrogen abstraction, k_r , and $k_i/(k_i + k_d)$, the efficiency for ring inversion.

Mechanism 3. Quantum efficiency controlled by excited state conformational equilibrium. If the reaction rate of conformer A is slow relative to its rate of formation, it can rapidly equilibrate⁸⁻¹⁰ with the unreactive conformers B and C. Under these conditions $k_d < k_i < k_{-i} > k_r$ and the quantum yield for reaction of ketone (**1a**) is governed by eq 3.¹¹

$$\Phi = \frac{\alpha k_r}{\alpha k_r + k_d} \quad (3)$$

According to this mechanism the low quantum efficiency for the reaction of ketone **1a** would be attributed to the small fraction of reactive conformer A in the excited state equilibrium.

In order to distinguish between mechanisms 1, 2, and 3, the quantum yields for reaction of the phenyl substituted derivatives of ketone **1a** (**1b-d**) were measured. Ring substituents are known to effect the reactivity of phenyl alkyl ketones,¹² and comparable effects would be expected in their cyclic analogs. Thus, substituents known to greatly enhance the triplet reactivity of valerophenone would be expected to enhance in a similar way the reactivity of cyclobutyl phenyl ketone (**1a**). However, if mechanism 1 with $k_r > k_{-i}$ or mechanism 2 is

(8) This process would not be unlikely since conformational equilibration of substituted cyclobutanes in the ground state has been estimated to occur very fast ($k_i, k_{-i} > 10^{10} \text{ sec}^{-1}$).^{9,10}

(9) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, p 248.

(10) J. B. Lambert and J. D. Roberts, *J. Amer. Chem. Soc.*, 87, 3891 (1965).

(11) P. J. Wagner in "Creation and Detection of the Excited State," Vol. I, Part A, A. A. Lamola, Ed., Marcel Dekker, New York, N. Y., 1971, p 191.

(12) P. J. Wagner, A. E. Kemppainen, and H. N. Schott, *J. Amer. Chem. Soc.*, 95, 5604 (1973).

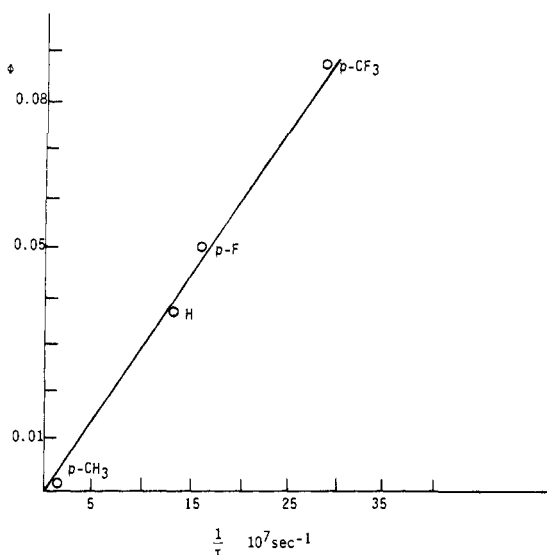


Figure 1. Maximum quantum yields¹³ for bicyclopentanol + ketone formation vs. triplet reactivities of substituted valerophenones.

operative, an enhancement in the triplet state reactivity of ketone **1a** would not result in a corresponding increase in quantum efficiency. This follows from eq 1 and eq 2 where the corresponding efficiencies for hydrogen abstraction ($k_r/k_r + k_{-i}$) and ($k_r/k_r + k_d$), would approximate unity. Alternatively, if mechanism 3 is correct or mechanism 1 with $k_r \approx k_{-i}$, the quantum yield for reaction of ketone **1a** would be directly related to its triplet state reactivity. From eq 3 mechanism 3 can be further distinguished from mechanism 1 with $k_r \approx k_i$. Under conditions where $\alpha k_r < k_d$, eq 3 predicts that the quantum yields for reaction of the substituted phenyl cyclobutyl ketones **1b–d** will be directly proportional to the triplet k_r values of the correspondingly substituted valerophenones. This does not hold for eq 1 and mechanism 1 with $k_r \approx k_{-i}$. Furthermore, under these conditions mechanism 3 predicts that the triplet lifetimes of ketones **1a–d** each being dominated by k_d will be comparable.

The quantum efficiencies for reaction of the phenyl substituted ketones **1b–d** were determined to be 0.001, 0.050, and 0.089, respectively.¹³ In addition the triplet lifetimes of ketones **1c–d** were determined from linear Stern–Volmer plots and were found to be in good agreement with the triplet lifetime of ketone **1a**.^{13,3e} A plot of the quantum yields vs. the triplet reactivity values of the correspondingly substituted valerophenones¹² is shown in Figure 1. The linear plot clearly demonstrates the direct relationship of quantum efficiency to triplet state reactivity in the cyclic ketone system (**1**) and

(13) All quantitative measurements were performed on degassed samples (three freeze–thaw cycles to 5×10^{-4} mm) mounted on a rotating merry-go-round apparatus with a central light source (internal water-cooled mercury arc lamp, Hanovia Type L-450 W). A filter solution consisting of 0.002 M potassium chromate and 1% potassium carbonate was used to isolate the 3130-Å mercury line.¹⁴ Benzophenone-benzhydrol actinometry¹⁵ was used for quantum yield determinations, and photoconversions were carried to 15% or less. Maximum¹⁶ quantum yields were determined on solutions consisting of 0.05 M ketone with added *tert*-butyl alcohol (0.05 M) in benzene (washed with sulfuric acid, dried, and distilled with phosphorus pentoxide). Quenching studies were performed using naphthalene.

(14) P. J. Wagner and G. Capen, *Mol. Photochem.*, **1**, 173 (1969).

(15) W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Amer. Chem. Soc.*, **83**, 2789 (1961).

(16) P. J. Wagner, I. E. Kochevar, and A. E. Kemppainen, *J. Amer. Chem. Soc.*, **94**, 7489 (1972).

verifies mechanism 3. From the slope of the curve, 3.3×10^{-10} sec, and eq 2, the fraction of reactive conformer A can be approximated. Correcting the slope downward for the larger k_r value (4×10^9) expected^{5,17} for conformer A relative to valerophenone decreases the slope to 1.2×10^{-11} . Using 1.3×10^6 as the value¹³ for k_d , the relative concentration of reactive conformer A is found to be 1.6×10^{-5} , and a pseudo-rate constant equal to 6.2×10^4 can be calculated for ketone **1a**. The calculated value is in excellent agreement with that measured for cyclobutylphenyl ketone **1a**.¹³ From Figure 1 pseudo-rate constants for the substituted phenyl cyclobutyl ketones (**1b–c**) are obtained which also show close agreement to the measured values.¹³

Figure 1 predicts nonphotoreactivity for *p*-methoxyphenyl cyclobutyl ketone (**1f**), and this in fact is observed. Ketone **1f** is found to undergo no detectable reaction after 4 days of irradiation.

We are investigating the solvolytic reactivity of the aryl bicyclo[1.1.1]pentanols produced in the above reactions and are exploring their synthetic utility as precursors to other highly strained ring systems.

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(17) F. D. Lewis, R. W. Johnson, and D. R. Kory, *J. Amer. Chem. Soc.*, **95**, 6470 (1973).

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Crystallographic Evidence for Copper–Copper Bonding at 2.8 Å. The Crystal and Molecular Structure of Tetrakis(tetraphenylphosphonium) Hexakis(1,2-dithiosquarato)octacuprate(I)

Sir:

Recently there has been much interest in metal cluster compounds and the bonding therein. In many cases it is difficult to unequivocally state that bonding interactions are present even when crystallographic structure determinations have been performed, due to the wide variance in both the bonded and nonbonded metal–metal distances. Additionally, theoretical criteria for invoking metal–metal bonding in clusters are generally vague.

In the case of copper(I) clusters, Cu–Cu distances as short as 2.38 Å in the (4-methyl-2-cupriobenzyl)dimethylamine tetramer¹ and as long as 3.45 Å in the “step” conformation of $[\text{Ph}_3\text{PCuBr}]_4$ ² have been observed. This latter distance is certainly nonbonded, but there are numerous other copper(I) cluster compounds with Cu–Cu distances which are intermediate between these two extremes.^{3–10}

(1) J. M. Guss, R. Mason, I. Sotofte, G. van Koten, and J. G. Noltes, *J. Chem. Soc., Chem. Commun.*, 446 (1972).

(2) (a) M. R. Churchill and K. L. Kalra, *J. Amer. Chem. Soc.*, **95**, 5772 (1973); (b) *Inorg. Chem.*, **13**, 1065 (1974).

(3) L. E. McCandlish, E. C. Bissell, D. Coucouvanis, J. P. Fackler, and K. Knox, *J. Amer. Chem. Soc.*, **90**, 7357 (1968).

(4) E. C. Bissell, Ph.D. Thesis, Case Western Reserve University, 1970, and references therein.