

Figure 2. Photoexcited acetone luminescence (curve a) and fluorescence (curve b). Acetone was 0.1 *M* in acetonitrile or Freon-113 at 3°. Intensities are uncorrected and in arbitrary units. Curve a was obtained by purging the solutions with nitrogen; curve b was obtained for aerated solutions containing 10<sup>-1</sup> *M* acrylonitrile. The intensity of the maximum of curve a is approximately three times that of curve b under comparable conditions; however, even higher intensities, corresponding to an increase in the contribution of acetone phosphorescence, can be achieved by vacuum degassing and rigorous solvent and solute purification.

controlled quencher of <sup>3</sup>K with negligible effect on the emission at 395 nm; (c) the quenching effect by O<sub>2</sub> is totally reversible, bubbling with nitrogen resulting in CAS, but purging with nitrogen after addition of 1,3-pentadiene does not bring back the CNS; (d) the intensity of 9,10-dibromoanthracene chemiluminescence which is activated mainly by triplet-singlet energy transfer is tremendously enhanced by nitrogen deoxygenation.

These results, in fact, suggested that acetone phosphorescence should be detected under the conventional spectrophotoluminescence conditions by simple deoxygenation of the sample by nitrogen bubbling. Indeed, we were gratified to find deoxygenation of acetonitrile solutions of acetone either with nitrogen purging or freeze-thaw cycles on a vacuum line allows ready detection of a new acetone photoluminescence (Figure 2). The lifetime of this emission was found to be of the order 2–20 μsec, depending on the thoroughness of degassing and purification of solvent and acetone. The effect of degassing on the photoluminescence of cyclohexanone (τ<sub>P</sub> ~ 3 μsec and limited by α cleavage<sup>7</sup>) is much less than for acetone and no effect of degassing was observed for cyclopentanone (τ<sub>P</sub> ~ 0.3 μsec).<sup>7</sup>

It is important to note that within the experimental error φ<sub>\*</sub><sup>T</sup> is ~0.5, calculated (eq 4) from the work reported here and the literature values of φ<sub>F</sub><sup>5</sup> and φ<sub>\*</sub><sup>S</sup>, and the inherent phosphorescent lifetime. This is the same value deduced from chemical titration of acetone triplets generated from thermolysis of 1.<sup>13</sup>

In conclusion, relatively intense acetone phosphorescence can be easily observed in fluid solution near room temperature by simple nitrogen degassing of solutions of 1 in acetonitrile and other photochemically "inert" solvents. This result opens many new and exciting

possibilities for study and use of alkanone phosphorescence in solution. In particular, contradictory conclusions<sup>23,24</sup> concerning the kinetics of acetone decay processes and photoreactions may now be resolved. For example, we have studied the Stern-Volmer quenching of the CNS of 1 by cyclohexane (10<sup>-2</sup>–0.5 *M*) in acetonitrile at 50° and obtained a linear quenching plot, with a slope of 2.7 *M*<sup>-1</sup>. The lifetime of acetone triplets at this temperature in acetonitrile was determined to be ~8 × 10<sup>-6</sup> sec by independent measurements by single photon counting. Thus, the rate constant for quenching of acetone triplets by cyclohexane is calculated to be 3.4 × 10<sup>5</sup> *M*<sup>-1</sup> sec<sup>-1</sup>. We feel that this value is in excellent agreement with a value (3.2 × 10<sup>5</sup> *M*<sup>-1</sup> sec<sup>-1</sup>) measured by the time delayed phosphorescence technique at 25°.

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(23) The status of the dynamics of acetone triplets is quite confusing since conflicting conclusions and evaluations of lifetimes appear in the literature. For example, "energy hopping" between acetone molecules has been invoked<sup>4</sup> to explain increasing Stern-Volmer quenching constants as one proceeds from hexane to acetone as solvent. This interpretation has been challenged<sup>24</sup> on the basis of new Stern-Volmer quenching data. The assumptions used to interpret the data have, in turn, been challenged as incorrect.<sup>5</sup>

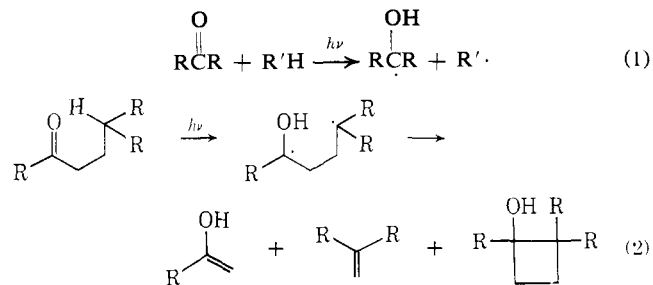
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### Entropic Control of the Photochemical Reactivity of Alkyl Phenyl Ketones<sup>1</sup>

Sir:

The inter- and intramolecular hydrogen abstraction reactions of carbonyl compounds (eq 1, 2) are among



the most extensively studied photochemical reactions.<sup>2</sup> The formation of the intermediate radical pair or 1,4-biradical is normally described in terms of transition-

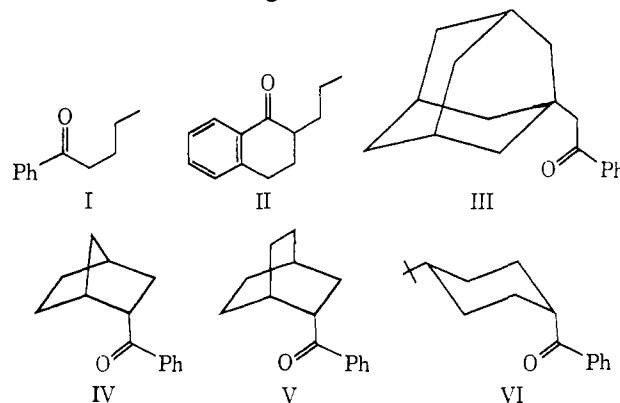
(1) The authors thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and PPG Industries for support of this research.

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state theory;<sup>2b, 3-6</sup> however, it has been suggested that the hydrogen transfer process should be treated as a radiationless transition.<sup>7-9</sup> The transition-state model adequately explains a variety of experimental observations including the dependence of lifetime upon the electronic state,<sup>10</sup> deuteration, and temperature<sup>11</sup> as well as the analogous behavior of carbonyl  $n, \pi^*$  excited states and alkoxy radicals.<sup>2</sup> A nonplanar transition state with minimized torsional strain has recently been postulated for intramolecular  $\gamma$ -hydrogen transfer.<sup>5,6,12</sup> In order to provide more detailed information about the transition state for intramolecular  $\gamma$ -hydrogen abstraction, we have investigated the photochemical behavior of a series of alkyl phenyl ketones (I-VI) having similar  $n, \pi^*$  triplet energies and  $\gamma$  C-H bond strengths, but differing in conformational mobility.<sup>13</sup> We wish to report that excited-state reactivity toward  $\gamma$ -hydrogen abstraction is dependent upon molecular conformation and that this dependence reflects entropic contributions to the transition state.

Table I summarizes quantum yield and kinetic data for ketones I-VI. The quantum yields for product formation are considerably larger in 8.9 *M* 1-propanol-benzene than in benzene.<sup>14,15</sup> Such solvent effects are

attributed to the ability of alcohol solvents to suppress biradical reversion to ground-state ketone.<sup>16</sup> In view



of the short triplet lifetimes for II-VI, it seems unlikely that radiationless decay competes with  $\gamma$ -hydrogen abstraction. Thus we assume that the quantum inefficiency for product formation is due to biradical reversion to ground-state ketone and that the triplet lifetime is determined by the rate of  $\gamma$ -hydrogen abstraction ( $1/\tau = k_\gamma$ ). The total variation in rate constant for ketones I-VI (80-fold) is much larger than that for tertiary *vs.* secondary  $\gamma$ -hydrogen abstraction in acyclic ketones (fourfold).<sup>2b</sup>

Possible explanations for the variation in rate constant with molecular structure include differing  $n, \pi^*$  triplet energies,  $\gamma$  C-H bond strengths,<sup>17</sup> or transition-state geometries. Variations in any of these parameters should influence the deuterium isotope effect for  $\gamma$ -hydrogen abstraction. Deuteration at the  $\gamma$  position of IV<sup>18</sup> results in a small increase in the quantum yield for product formation and a decrease in rate constant for  $\gamma$ -hydrogen abstraction (Table II). The kinetic isotope effect for IV is similar to that obtained by Wagner<sup>20</sup> for nonanophenone ( $k_H/k_D = 4.8$ ), an adequate model for valerophenone (I).<sup>21</sup> The similarity

**Table I.** Quantum Yield<sup>a</sup> and Kinetic Data for Alkyl Phenyl Ketones

Ketone	Solvent	$\Phi_{elim}$	$\Phi_{ey}$	$k_q\tau$ , $M^{-1}b$	$k_\gamma \times 10^8$ , $sec^{-1}$
I <sup>c</sup>	C <sub>6</sub> H <sub>6</sub>	0.33	0.07	40	1.2
	<i>t</i> -BuOH	1.00			
II	C <sub>6</sub> H <sub>6</sub>	0.09	0.03	8.5	5.9
	PrOH	0.36	0.03		
III	C <sub>6</sub> H <sub>6</sub>		0.14	5.5	9.2
	PrOH		0.34		
IV <sup>d</sup>	C <sub>6</sub> H <sub>6</sub>	0.10		0.7	70
	PrOH	0.16			
V <sup>d</sup>	C <sub>6</sub> H <sub>6</sub>	0.041		0.5	100
	<i>t</i> -BuOH	0.058			
VI <sup>e</sup>	C <sub>6</sub> H <sub>6</sub>	0.024		0.7	70
	PrOH	0.098			

<sup>a</sup> Quantum yields for elimination and cyclization products measured at  $23 \pm 2^\circ$  in degassed benzene or 8.9 *M* 1-propanol-benzene solvent. <sup>b</sup> Slopes of linear Stern-Volmer plots using 1,3-pentadiene,  $k_q = 5.0 \times 10^9 M^{-1} sec^{-1}$ . <sup>c</sup> Data from ref 6, total quantum yield in *tert*-butyl alcohol 1.00. <sup>d</sup> Data from ref 5. <sup>e</sup> Data from ref 13b.

**Table II.** Deuterium Isotope Effects on  $\gamma$ -Hydrogen Abstraction for *endo*-2-Benzoylnorbornane<sup>a</sup>

Ketone	$\Phi$	$k_q\tau$ , $M^{-1}$	$k_\gamma \times 10^8$ , $sec^{-1}$	$k_H/k_D$
IV-h	0.11	0.92	34.0	
IV-d	0.16	3.4	8.6	$4.0 \pm 0.2$

<sup>a</sup> Values in cyclooctane solvent at  $20^\circ$ ,  $k_q = 3.2 \times 10^9 M^{-1} sec^{-1}$ .

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(15) The quantum yields increase continuously with added 1-propanol even at the highest concentration of 1-propanol employed (8.9 *M*).

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(21) Nonanophenone and valerophenone (I) have similar quantum yields and rate constants for  $\gamma$ -hydrogen abstraction.<sup>20</sup> The kinetic isotope effects for both nonanophenone and IV are a composite of primary and secondary effects. The magnitude of the secondary deuterium isotope effect is currently under investigation.

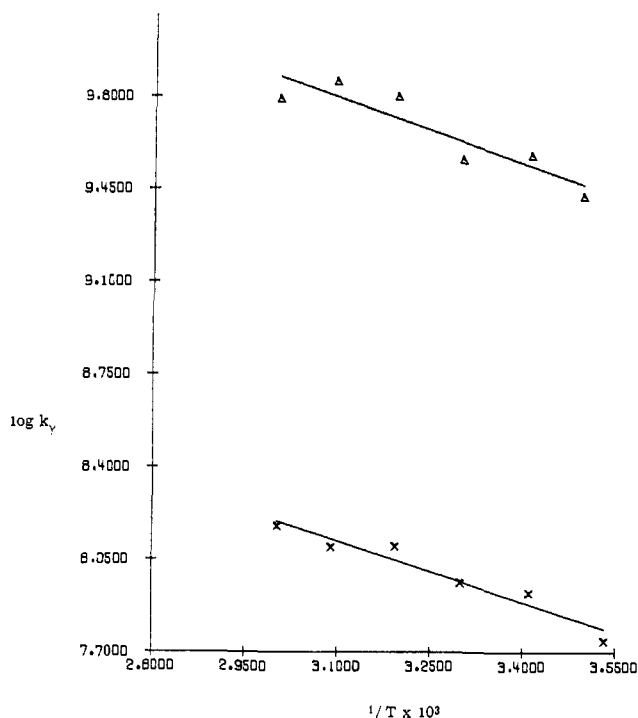


Figure 1. Plot of  $\log k_{\gamma}$  vs.  $1/T$  for valerophenone (I, X) and endo-2-benzoylnorbornane (IV,  $\Delta$ ).

of the kinetic isotope effects indicates that the large difference in reactivity between I and IV cannot be due to differences in  $\gamma$  C-H bond strength or the geometry of the transition state. In addition, possible contributions of tunneling to the rate constant must be similar for I and IV.<sup>22</sup> The magnitude of the isotope effects indicates moderate C-H bond breaking in the transition state.<sup>23</sup>

The variation in rate constant with molecular structure for ketones I-VI suggests that the contributions of internal rotations to the entropies of activation may be responsible for the observed rate enhancements. The rate factors of 5-8 for each additional internal rotation which must be frozen out in the transition state is in good accord with recent predictions for strain-free six-membered transition states.<sup>24</sup> In order to evaluate the contributions of entropy to the transition state, Arrhenius parameters for I and IV were evaluated. Rate constants for  $\gamma$ -hydrogen abstraction were determined between 10 and 70° by Stern-Volmer quenching using 1,3-pentadiene in cyclooctane solvent.<sup>25</sup> The resulting Arrhenius plots are shown in Figure 1. The activation energies for I ( $3.5 \pm 0.5$  kcal/mol) and IV ( $3.7 \pm 0.9$  kcal/mol) are the same. However, the entropy of activation for I ( $-12.5 \pm 1.5$  eu) is much more negative than that for IV ( $-4.0 \pm 2.8$  eu).<sup>26</sup> Thus the large difference in reactivity between I and IV is primarily due to entropic contributions to the transition state

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(26) Entropies of activation calculated for 25°. Errors are standard deviation from least square.

which result from the two fewer rotational degrees of freedom which must be frozen out for IV.

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### Direct Evidence for Charge Localization in Pyrazine-Bridged Mixed-Valence Ruthenium Complexes

Sir:

More than four years ago, Creutz and Taube<sup>1</sup> reported on the electronic spectra of binuclear pentammine ruthenium complexes  $[(\text{NH}_3)_5\text{Ru}(\text{pyr})\text{Ru}(\text{NH}_3)_5]^{4+.5+.6+}$  (pyr = pyrazine), in which an absorption band observed in the +5 mixed valence [Ru(II), Ru(III)] species and absent in the spectra of the +4 and +6 ions, was assigned as an intervalence charge-transfer transition corresponding to the process [Ru(II), Ru(III)]  $\rightarrow$  [Ru(III), Ru(II)]\*. Such an assignment, requiring essentially distinct valences localized on otherwise equivalent metal sites, has stimulated several theoretical analyses<sup>2-4</sup> and numerous experimental studies involving a variety of techniques, including nmr,<sup>3</sup> Raman,<sup>5</sup> Mössbauer,<sup>6</sup> and absorption<sup>7</sup> spectroscopies. The results of these investigations are either only suggestive or inconclusive and are, in some cases, in conflict. Further questions about the assignment have been introduced from the work of Adeymi, *et al.*,<sup>8</sup> in which an analogous charge-transfer band in the related systems  $[\text{Cl}(\text{bipy})_2\text{Ru}(\text{pyr})\text{Ru}(\text{bipy})_2\text{Cl}]^{2+.3+.4+}$  (bipy = bipyridine) was not observed. The implications of understanding both these systems in terms of electron exchange and metal-ligand interactions have been emphasized<sup>7</sup> and clearly warrant the elucidation of the charge distributions needed to explain the observed phenomena. In this communication we report direct evidence of the charge distributions in both the pentammine and bipyridine ruthenium complexes using X-ray photoelectron spectroscopy. This technique is well suited for such an investigation because it monitors electron distributions rapidly ( $\sim 10^{-17}$  sec) and unambiguously through inspection of so-called chemical shifts.<sup>9</sup>

All data were taken with a HP 5950A ESCA spectrometer which provides high-resolution low-background data by virtue of the relatively monochromatic Al K $\alpha$  X-radiation used for photoejection. The working pressure in the sample analyzing region was no greater than  $5 \times 10^{-9}$  Torr, thus further simplifying data analysis through reduction of spurious sample

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