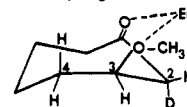


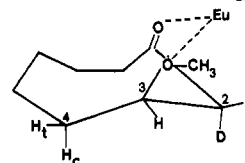
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- (16) Irradiation of 4 in an inert solvent such as cyclohexane gave dimers whose structures and mechanism of formation will be discussed in a separate paper.
- (17) For related systems with $J_{\text{trans}} > J_{\text{cis}}$, see S. Kabuss, H. G. Schmid, H. Friebohn, and W. Faisst, *Org. Magn. Reson.*, 1, 451 (1969); M. St.-Jacques and C. Vaziri, *ibid.*, 4, 77 (1972).
- (18) The coupling constants were slightly different from those of the corresponding protio compounds, to an extent definitely outside the experimental error.
- (19) For other examples of this effect, see G. V. Smith, W. A. Boyd, and C. C. Hinckley, *J. Am. Chem. Soc.*, 93, 2417 (1971); J. K. M. Saunders and D. H. Williams, *J. Chem. Soc., Chem. Commun.*, 436 (1972).
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- (21) Analyzed by NMR using the same methods as for the photoinduced additions. NMR integration, using the methoxy protons as a reference, showed that a small fraction of the C_2 proton cis to the methoxy was exchanged, but the product is mainly 3- d_3 .
- (22) In this case, \sim 50% of the C_7 proton cis to the methoxy is also exchanged, owing to the slowness of the addition and the prolonged opportunity for the product to exchange.
- (23) One cannot, however, strictly rule out the possibility that some fraction of the reaction of 1 with methanol may proceed by polar addition to a photoexcited state.
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- (25) The addition of CH_3COOD to *trans*-cyclooctene occurs in a stereospecific syn manner, for which a concerted six-centered transition state has been suggested: K. T. Burgoine, S. G. Davies, M. J. Peagram, and G. H. Whitham, *J. Chem. Soc., Perkin Trans. 1*, 2629 (1974).
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- (28) The same is true for Z', another reason why we favor the synchronous addition, $T \rightarrow Z \rightarrow P$.
- (29) The stereochemistry of Michael additions has not been studied in detail, but examples of syn addition, anti addition, and nonstereoselective addition are known. For brief discussions, see S. Patai and Z. Rappoport in "The Chemistry of Alkenes", S. Patai, Ed., Wiley-Interscience, New York, N.Y., 1964, p 464; see also R. A. Abramovitch, M. M. Rogič, S. S. Singer, and N. Venkatesevaran, *J. Org. Chem.*, 37, 3577 (1972), and references therein.
- (30) All analyses were by Spang Microanalytical Laboratory, Ann Arbor, Mich.
- (31) For numbering, see structure in the text. Spectra were determined on a Varian HA 100 instrument, and all assignments were confirmed by decoupling.
- (32) In a control experiment, no adduct could be detected in the absence of light.
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- (34) E. W. Garbisch, Jr., *J. Org. Chem.*, 30, 2109 (1965).
- (35) Many such spectra were recorded, with varying ratios of substrate to shift reagent.
- (36) These results are consistent with a rigid geometry for the europium complex,¹³ with large *trans* coupling constants for $J_{H_2, H_3} = 8.0$ Hz and $J_{H_3, H_4} = 7.5$ Hz and a small *cis* coupling constant, $J_{H_2, H_6} = 2.0$ Hz. Consistent with this, J_{H_2, H_3} in the unlabeled complex is small (2.0 Hz).¹³
- (37) H. Houp and G. H. Whitham, *J. Chem. Soc. B*, 164 (1966).
- (38) These results are consistent with a rigid geometry for the europium complex,¹³ with large *trans* coupling constants, $J_{H_2, H_3} = 8.0$ Hz and $J_{H_3, H_4} = 8.0$ Hz, and a small *cis* coupling constant, $J_{H_3, H_6} = 3.0$ Hz. Consistent with this conclusion is the small value (3.0 Hz) observed for J_{H_{2c}, H_3} in the unlabeled ketone.¹³



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(37) H. Houp and G. H. Whitham, *J. Chem. Soc. B*, 164 (1966).

(38) These results are consistent with a rigid geometry for the europium complex,¹³ with large *trans* coupling constants, $J_{H_2, H_3} = 8.0$ Hz and $J_{H_3, H_4} =$



8.0 Hz, and a small *cis* coupling constant, $J_{H_3, H_6} = 3.0$ Hz. Consistent with this conclusion is the small value (3.0 Hz) observed for J_{H_{2c}, H_3} in the unlabeled ketone.¹³

Substituted Acetophenones. Importance of Activation Energies in Mixed State Models of Photoreactivity

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Abstract: The photoabstraction and phosphorescence of triplet acetophenones requires a mixing between zero-order n, π^* and π, π^* states with interaction energies $\geq 100 \text{ cm}^{-1}$. The extent of mixing (b^2) and the energy separation (ΔE) of the resultant states are fundamental properties of the molecule and are independent of the phenomena being observed. However, the best expressions for the radiative rate constants (eq 1) and for the reaction rate constants (eq 6) differ since no activation energies are involved in the former while there are substantial barriers to reaction in the latter. Variations in photoreactivity between compounds are then mainly manifested as activation energy differences and the reactivity of a given compound changes significantly with temperature. On the other hand the radiative rate constants show essentially no temperature dependence although they do differ widely from compound to compound.

Introduction

Considerable experimental and theoretical activity has gone into trying to determine the factors which influence the

photoreactivity of carbonyls with respect to hydrogen abstraction (k_a), $>\text{C}=\text{O}^* + \text{RH} \rightarrow >\text{C}\text{OH} + \text{R}\cdot$. Yang and co-workers¹⁻³ have shown that the variations in the reactivities

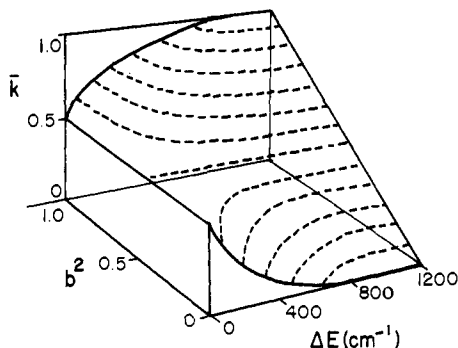


Figure 1. Reactivity surface at 300 K as a function of b^2 , the fractional n, π^* character of T_1 , and of ΔE , the gap between T_2 and T_1 . The contours join points of equal reactivity.

of a series of acetophenones at room temperature can be correlated with the proportion of n, π^* character admixed in the lowest triplet states (T_1) as measured by the radiative lifetimes (τ_{rad}) in low-temperature glasses. Wagner⁴⁻⁶ pointed out that T_1 and T_2 might still be essentially pure π, π^* and n, π^* , reactivity variation being associated with varying thermal population, i.e., Boltzmann factors, resulting from differing ΔE ($=E_{T_2} - E_{T_1}$). In the most general case one might envisage T_1 and T_2 as states with mixed n, π^* and π, π^* characters lying sufficiently close together such that Boltzmann factors might also be important.⁶

Recently extensive physical measurements at low temperatures have provided further evidence for a mixed state description for the triplet states of aromatic carbonyls and have shown that the amount of mixing can vary not only from molecule to molecule but also depends markedly upon the environment.⁷⁻¹⁴ It can be rather confusing to envisage variations in reactivity as ΔE and/or mixing vary. In this paper it is shown how such variations can be considered in terms of a reactivity surface. This leads to a method of treating the data which allows estimations of the relative importance of mixing and of Boltzmann factors. Finally examination of the model suggests refinements which appear to be in general accord with experiment.

Results and Discussion

Models. We shall first develop the model along standard lines.^{6,7} Consider a molecule in which states T_1 and T_2 can be regarded as mixed states of two zero-order states n, π^* and π, π^* such that $\psi_{T_1} = b\psi_{n, \pi^*} + \sqrt{(1-b^2)}\psi_{\pi, \pi^*}$ and $\psi_{T_2} = \sqrt{(1-b^2)}\psi_{n, \pi^*} - b\psi_{\pi, \pi^*}$ where b^2 is the fractional n, π^* character associated with T_1 . It is further assumed that reactivity of a state be associated with its fractional n, π^* character so that $k_{T_1} = b^2 k_{n, \pi^*}$ and $k_{T_2} = (1-b^2)k_{n, \pi^*}$. In general the observed overall rate constant k is the sum of the individual rate constants, k_i , for the states weighted by the fraction of molecules in the respective states, f_i . Specifically for the two-state system under consideration here

$$k(b^2, \Delta E, T) = \sum_i k_i f_i = k_{n, \pi^*} \frac{b^2 + (1-b^2)e^{-\Delta E/RT}}{1 + e^{-\Delta E/RT}} \quad (1)$$

where $\Delta E = E_{T_2} - E_{T_1}$.

Figure 1 shows a plot of the relative rate constant \bar{k} ($=k/k_{n, \pi^*}$) as a function of b^2 and ΔE for a temperature of 300 K. The reactivity of a given system is then represented by the corresponding point on the reactivity surface. The surface will be the same for other temperatures except that the ΔE scale is expanded by a factor of $(T/300)$; i.e., for a given b^2 and a temperature of 77 K, \bar{k} will have the same value at $\Delta E = 154 \text{ cm}^{-1}$ as it had at $\Delta E = 600 \text{ cm}^{-1}$ when the temperature is 300 K. The question then arises whether the points representing a series of reactants are simply scattered on the reactivity

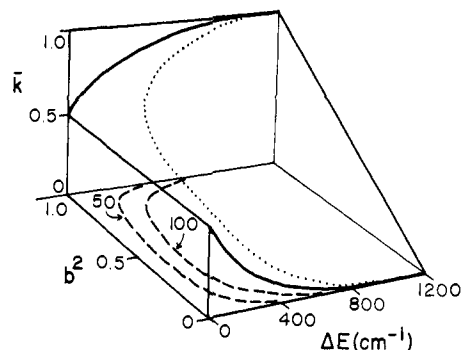


Figure 2. Reactivity surface: on the b^2 - ΔE plane, b^2 is plotted as a function of ΔE , for interaction energies of 50 and 100 cm^{-1} . The resultant reactivity pathway (\cdots) for $|V| = 100 \text{ cm}^{-1}$ is also shown on the reactivity surface.

surface or whether they are grouped in some simple systematic fashion.

Let \mathcal{H}_0 and \mathcal{H} ($=\mathcal{H}_0 + v$) be the Hamiltonians associated with the zero-order states and with the "real" states T_1 and T_2 , respectively, where v is the perturbation causing the mixing. It can readily be shown that

$$\Delta E = E_{T_2} - E_{T_1} = (1 - 2b^2)(\Delta E^\circ + \Delta K) - 4b\sqrt{(1-b^2)}V \quad (2)$$

In the above $\Delta E^\circ = E_{n, \pi^*} - E_{\pi, \pi^*}$ where E_{n, π^*} and E_{π, π^*} are the energies of the zero-order states under \mathcal{H}_0 , while $K_{n, \pi^*} = \langle \psi_{n, \pi^*} | v | \psi_{n, \pi^*} \rangle$ and $K_{\pi, \pi^*} = \langle \psi_{\pi, \pi^*} | v | \psi_{\pi, \pi^*} \rangle$ are small energy terms whose difference ΔK can generally be neglected. $V = \langle \psi_{n, \pi^*} | v | \psi_{\pi, \pi^*} \rangle$ is the interaction energy between the zero-order states, the absolute value of which has been estimated by Hirota⁷ to be $\sim 100 \text{ cm}^{-1}$ for a wide range of aromatic carbonyls. This value is reasonable for a vibronic interaction. When b^2 is small, then by first-order perturbation theory $b \approx |V|/\Delta E^\circ$, while, when b^2 is close to unity, $\sqrt{(1-b^2)} \approx -|V|/\Delta E^\circ$. Fortunately in the region where the above approximations are not so good the second term, $4b\sqrt{(1-b^2)}V$, in eq 2 makes a dominant contribution to ΔE and so

$$\Delta E \approx \left[\frac{1-2b^2}{b} + 4b\sqrt{1-b^2} \right] \times |V| \text{ for } b^2 < 0.5 \quad (3)$$

$$\Delta E \approx 2|V| \text{ for } b^2 = 0.5 \text{ (zero-order states degenerate)} \quad (4)$$

$$\Delta E \approx \left[\frac{2b^2-1}{\sqrt{(1-b^2)}} + 4b\sqrt{(1-b^2)} \right] \times |V| \text{ for } b^2 > 0.5 \quad (5)$$

Thus for a given $|V|$, ΔE can be obtained as a function of b^2 and correspondingly specific values for \bar{k} can be calculated as ΔE and b^2 vary as prescribed by eq 3-5. Figure 2 shows ΔE plotted as a function of b^2 for $|V| = 50$ and 100 cm^{-1} and also the resultant map of \bar{k} for $|V| = 100 \text{ cm}^{-1}$. It is evident that for reasonable $|V|$ values the reactivity points lie on a fairly well-defined pathway on the upper surface. It is important to stress that Boltzmann effects, which rely only on ΔE , and mixing effects, which depend on b^2 , should not be considered as independent quantities since changes in ΔE result in concomitant changes in b^2 and vice versa.

The above model can now be expressed in a form which allows an estimate to be made of the degree of mixing. For a given $|V|$, values of ΔE are obtained as b^2 is varied from 0 to 1 using eq 3-5. These values of ΔE and b^2 are then substituted into eq 1 to obtain values of \bar{k} at two temperatures. In this way the reactivity at one temperature can be graphed as a function of the reactivity at another temperature. This has been done in Figure 3 for temperatures of 300 and 77 K.

Consider first the case of no mixing; i.e., $|V| = 0 \text{ cm}^{-1}$.

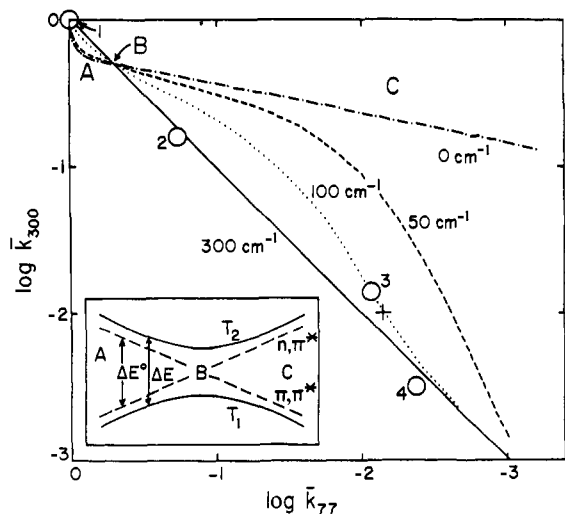


Figure 3. Relative reactivity at 300 K as a function of the relative radiative constants or reactivity at 77 K for interaction energies of 0, 50, 100, and 300 cm^{-1} using eq 1. The experimental points (O) are from ref 2. The inset diagram shows the energy levels of the states corresponding to the three regions A, B, and C in the main diagram. 1 represents *p*-trifluoroacetophenone; 2, acetophenone; 3, *p*-methylacetophenone; 4, 3,4-dimethylacetophenone.

When n, π^* is lowest (region A of diagram), thermal excitation to the upper π, π^* state decreases the population in the reactive n, π^* state. Since this effect is more pronounced at higher temperatures, the higher temperature reactivity, \bar{k}_{300} , falls off more rapidly than the low temperature reactivity, \bar{k}_{77} . At B the n, π^* and π, π^* states are degenerate. Here there is a 50% population in n, π^* at all temperatures so that both \bar{k}_{300} and \bar{k}_{77} decrease by a factor of 2. In region C, the upper state is the n, π^* state accessible by thermal population so that the high temperature reactivity, \bar{k}_{300} , falls off less rapidly than the low temperature reactivity, \bar{k}_{77} .

In the other limiting situation of $|V|$ large, the real states T_2 and T_1 never approach closely since they can never come closer in energy than $2|V|$. This means that the reactivity is only dependent on the nature of the lowest state since the upper state is thermally inaccessible. In Figure 3 the straight line with slope of -1 describes this situation, namely, that \bar{k}_{77} and \bar{k}_{300} behave identically as the lowest state changes from n, π^* to π, π^* in nature. It is interesting that for $|V| \geq 300 \text{ cm}^{-1}$ the curves are indistinguishable from this limiting case.

It is difficult to measure chemical reactivities at 77 K. However, since the oscillator strength of a radiative transition is dependent on the n, π^* character of the triplet carbonyl, it is reasonable to assume that radiative rate constants \bar{k}_{rad} , should also obey a relationship similar to that described by eq 1. In Figure 3, reactivity data at room temperature obtained by Yang et al.² is plotted vs. radiative rate constants at 77 K. It is apparent that a model which simply involves Boltzmann effects, i.e., the thermal population of close-lying triplets without any mixing, cannot explain both the room-temperature reactivity and the low-temperature radiative lifetimes. It should also be noted that only when T_1 has little n, π^* character (region C in Figure 3), do the curves for different $|V|$ values deviate significantly enough from one another to enable meaningful distinctions.

By using a reasonable value of $|V|$ the model can be made to reflect the experimental trends (Figure 3). However the reactivity of a state is assumed to depend solely on its n, π^* character. The inset in Figure 3 shows that, when b^2 is small (region C), T_1 lies about ΔE lower in energy than the zero-order n, π^* state. The rate constant k_{T_1} is written as $b^2 k_{n, \pi^*} = b^2 A e^{-E_{n, \pi^*}^a / RT}$ where E_{n, π^*}^a is the

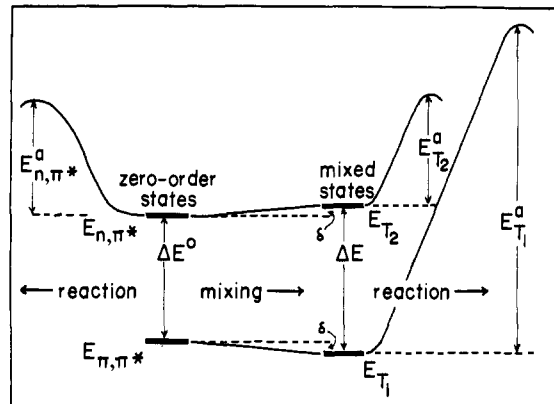


Figure 4. Comparison of reaction from a pure n, π^* state with reaction from the two mixed states T_1 and T_2 to show possible activation energy differences.

activation energy associated with a pure n, π^* state. Therefore, $k_{T_1} = A e^{-(E_{n, \pi^*}^a + \theta) / RT}$ where $\theta = -RT \ln b^2$. For example, for $b^2 = 0.007$ and $T = 300 \text{ K}$ this gives $\theta = 1034 \text{ cm}^{-1}$, but for $b^2 = 0.007$ and $|V| = 100 \text{ cm}^{-1}$, $\Delta E = 1212 \text{ cm}^{-1}$. Thus the model in fact predicts that the height of the reaction barrier for T_1 , which is largely π, π^* in nature, lies below that of the pure n, π^* state. This seems unreasonable and arises because the model does not allow for additions to the activation energies stemming from variation in the energies of T_1 and T_2 with respect to the pure n, π^* state. One way to do this is to introduce additional energy terms reflecting the displacements of T_1 and T_2 from the zero-order n, π^* state so that individual rate constants are now $k_{T_1} = b^2 k_{n, \pi^*} e^{-(\Delta E - \delta) / RT}$ and $k_{T_2} = (1 - b^2) k_{n, \pi^*} e^{\delta / RT}$ (Figure 4). The overall abstraction rate constant becomes

$$k_a(\delta, \Delta E, T) = \frac{k_{T_1} + k_{T_2} e^{-\Delta E / RT}}{1 + e^{-\Delta E / RT}} = \frac{k_{n, \pi^*} e^{-(\Delta E - \delta) / RT}}{1 + e^{-\Delta E / RT}} \quad (6)$$

Mixing terms do not appear explicitly in eq 6, but it should be remembered that ΔE and δ both depend upon V and b^2 . Also since there is no evidence for energy dependence in radiative processes, the first model, eq 1, should still apply for k_{rad} .

Although the changes may appear to be modest, the two models are quite different in their predictions as to the origin of reaction. For example, according to the first model for $|V| = 100 \text{ cm}^{-1}$ and $b^2 = 0.007$, $\Delta E = 1212 \text{ cm}^{-1}$, and $\bar{k}_{a, 300} = 0.01$. This is the point shown as a cross in Figure 3. Equation 1 shows that only 30% of reaction originates from T_2 despite the fact that the latter carries 99% of the n, π^* character. On the other hand, when $V = 100 \text{ cm}^{-1}$ and $b^2 = 0.012$, we obtain $\Delta E = 960 \text{ cm}^{-1}$, $\delta = 9 \text{ cm}^{-1}$, and, according to eq 6, $\bar{k}_{a, 300}$ is again 0.01, but the second model predicts that 99% of the reaction should originate from T_2 . This is because the higher barrier now associated with T_1 effectively blocks reaction from this state (Figure 4). A high activation energy for a state that is essentially π, π^* in character seems quite reasonable. Despite these apparent differences both models predict decreasing reactivity as the π, π^* character of T_1 increases, and, if a value of $\sim 100 \text{ cm}^{-1}$ is used for the interaction energy, eq 6 and 1 for $\bar{k}_{a, 300}$ and $\bar{k}_{\text{rad}, 77}$, respectively, still afford a good fit with Yang's experimental data.

However, experimentally determinable differences between the models are manifested if the temperature dependences of the reactivities, rather than simply the reactivities at a given temperature, are compared. Model 1 results in rate differences showing up mainly in the temperature independent part, or A factor, of an Arrhenius-type equation ($k_a = A e^{-E_a / RT}$). For example, the A factor for $\bar{k}_{a, 300} = 0.01$ when $|V| = 100 \text{ cm}^{-1}$ is 20 times smaller than the A factor associated with $\bar{k}_{a, 300} =$

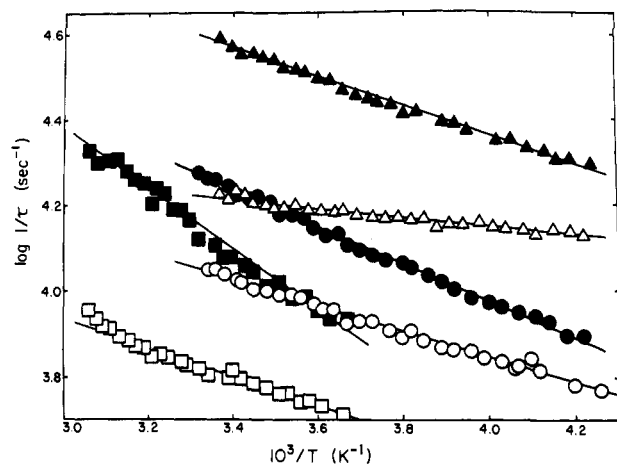


Figure 5. Variation in the lifetimes of triplet acetophenone in the absence, open points, and presence of cyclohexane, closed points, as a function of temperature: (Δ) 1×10^{-4} M *p*-trifluoromethylacetophenone, (\blacktriangle) with 1.0×10^{-2} M cyclohexane; (O) 1×10^{-4} M acetophenone, (\bullet) with 1.5×10^{-2} M cyclohexane; (\square) 1×10^{-4} M *p*-methylacetophenone, (\blacksquare) with 0.25 M cyclohexane. Solvent was acetonitrile.

1.0, while the exponential term decreases only 5-fold. On the other hand as can be seen from eq 6 the second model predicts that reactivity differences show up almost totally in the exponential term, i.e., activation energy.

Results

In order to see which model predicted the experimental behavior best, absolute rate determinations for abstraction by three acetophenones were carried out over a range of temperatures. Yang and Dusenbery² employed 2-propanol (in benzene) as the hydrogen donor and had variable amounts of *cis*-1,3-pentadiene present as quencher. In this study acetonitrile was used as solvent because it affords both ready solubility of the compounds and also long phosphorescence lifetimes in the temperature range under consideration.¹⁵ Two hydrogen donors were employed, 2-propanol to form a link with Yang's work and cyclohexane in case there were any unexpected polar effects with 2-propanol. Typical data are given in Table I and Figure 5. The changes in rate constant for 2-propanol follow almost exactly those reported by Yang, while it is obvious that reactivity differences are mainly associated with activation energy changes as predicted by the second model.

Some further points may be made. As noted above, in the case of the second model, when T_1 is predominantly π, π^* in character, reaction originates mainly from the upper state. However, it is important to realize that this comes about not simply from the high n, π^* character of T_2 but also because of the higher energy barrier to reaction from T_1 . In contrast, as shown above, in the first model significant reaction can occur from T_1 even though it is largely π, π^* .

If it is assumed that reaction arises simply from a pure n, π^* state displaced by ΔE° from a π, π^* state (see Figure 4), we obtain

$$k = \frac{k_{n,\pi^*} e^{-\Delta E_0/RT}}{1 + e^{-\Delta E_0/RT}} \quad (7)$$

With reference to eq 6, when $b^2 \ll 0.5$ we have $\delta \ll \Delta E$; thus over much of the reaction surface the forms of eq 6 and 7 are in fact quite similar. In these regions a model which neglects mixing is quite adequate to explain chemical reactivity in the room temperature region. This point of view has been emphasized very successfully recently by Wagner.¹⁶ From the above it is seen to be the natural consequence of a mixed state model in which activation energy difference between the states

Table I. Arrhenius Parameters for the Interaction Rate Constants of Acetophenone with Cyclohexane and 2-Propanol

| Ketone | [RH], ^a M | $10^{-5}k_a$, M ⁻¹ s ⁻¹ at | | E_a , kcal/mol | Log <i>A</i> |
|---------------------------------------|----------------------|---|-------------|---------------------|--------------|
| | | 293 K | | | |
| <i>p</i> -Trifluoromethylacetophenone | 0.010 (C) | 20.4 | 2.91 ± 0.05 | 8.48 ± 0.04 | |
| Acetophenone | 0.015 (C) | 3.9 | 3.54 ± 0.09 | 8.23 ± 0.07 | |
| <i>p</i> -Methylacetophenone | 0.250 (C) | 0.23 | 4.76 ± 0.02 | 7.91 ± 0.13 | |
| <i>p</i> -Trifluoromethylacetophenone | 0.001 (I) | 88.0 | 1.12 ± 0.12 | 7.78 ± 0.11 | |
| Acetophenone | 0.010 (I) | 21.3 | 1.69 ± 0.05 | 7.59 ± 0.05 | |
| <i>p</i> -Methylacetophenone | 0.100 (I) | 0.67 | 3.52 × 0.07 | 7.45 ± 0.06 | |

^a C ≡ cyclohexane; I ≡ 2-propanol.

Table II. Comparison of Radiative Lifetimes at 298^a and 77 K^b

| Ketone | τ_{rad}^{298} , ms | τ_{rad}^{77} , ms |
|---------------------------------------|-------------------------|------------------------|
| <i>p</i> -Trifluoromethylacetophenone | 3.8 | 2.4 |
| Acetophenone | 7.3 | 5.4 |
| <i>p</i> -Methylacetophenone | 90 | 138, 49 |

^a This work, solvent acetonitrile. ^b References 1, 2, 20.

is also taken into account. In studying a series of valerophenones at room temperature Wagner obtained rate constants which changed by a factor of 10 for $(E_{n,\pi^*} - E_{\pi,\pi^*}) \sim 1.5$ kcal mol⁻¹.¹⁶ Our model also indicates the same variation in *k* with ΔE . This does not mean that we can compare similar members of the series absolutely, e.g., acetophenone with valerophenone or 4-methylacetophenone with 4-methylvalerophenone. Both the kinetic and spectroscopic evidence indicate that acetophenone is of mixed character, whilst valerophenone appears to be almost pure n, π^* in nature.¹⁶ Also in going from valerophenone to 4-methylvalerophenone the rate drops by a factor of 7 while the drop is much larger for 4-methylacetophenone in comparison with acetophenone.

Radiative rate constants also show a marked variation with n, π^* in character, but, in contrast to abstraction rates, show little temperature variation (Table II). Since there is no evidence for activation energies, eq 1, rather than 6, should apply. This is easily confirmed. Using the parameters employed above, viz., $V = 100$ cm⁻¹, $b^2 = 0.01$, $\Delta E = 960$ cm⁻¹, and $\delta = 9$ cm⁻¹, eq 1 yields $\log \bar{k}_{rad} - 1.9$ at 77 K and -1.7 at 300 K, a twofold variation. On the other hand eq 6 yields $\log \bar{k}_{rad} - 7.8$ at 77 K and -2.0 at 300 K, a variation of almost a million. It should also be noted that the point to which the above calculations refer (cross in Figure 3) lies very close to *p*-methylacetophenone. Gallivan¹⁷ has reported an experimental value of ~ 1000 cm⁻¹ for ΔE for this compound in nice agreement with the calculated value.

Finally, the low values of the activation energies emphasize how reactive triplet carbonyls are. In fact the activation energies are as low as those associated with the reactions of reactive atoms like Cl· and F·. That the absolute rates of the carbonyls are lower stems largely from their lower *A* factors. This is to be expected on the basis of the greater complexity of the triplet reactants.¹⁸

Experimental Section

Materials. Acetonitrile (Burdick and Jackson) was carefully distilled before use. Cyclohexane (Spectroquality, MCB) was used as supplied, while 2-propanol was purified by preparative GC using an 8-ft 20% 20M Carbowax column with H₂ as carrier gas. Acetophenone (Fisher Scientific), *p*-methylacetophenone (Eastman Organic), and

p-trifluoromethylacetophenone (Columbia Organic) were further purified by trap-to-trap distillation under vacuum immediately before use.

Kinetic Studies. A general description of the lifetime apparatus has already been given.¹⁵ The measurements were carried out over a temperature range using the brass block thermostat already described.¹⁸ Above ambient temperatures were reached by means of heating coils imbedded in the block, while low temperatures were obtained by passing cold nitrogen through a series of channels cut in the block. Because of the large heat capacity of the block, temperatures accurate to 0.05 °C could easily be obtained. A small section of the emission cell protruded from the block and this volume was kept a few degrees warmer than the block temperature to minimize any distillation. The filter system for all three ketones was the same, i.e., excitation 7–54, emission 3–72 and 4–96 in series (Corning).

Emission Spectra and Quantum Yields. Spectra and quantum yield data were obtained using a Hitachi MPF-4 spectrofluorimeter and quinine bisulfate as a quantum yield standard.¹⁹ Radiative lifetimes were determined by measuring both the lifetimes and the quantum yields of emission of the samples ($\tau_{\text{rad}} = \tau/\varphi_{\text{em}}$).

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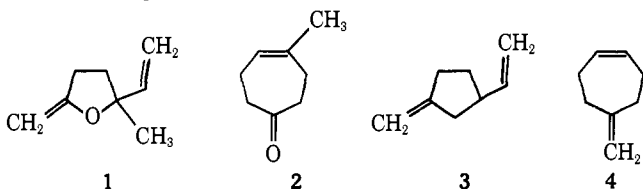
Interconversion of 1-Methylene-3-vinylcyclopentane and 5-Methylenecycloheptene. A Cope Rearrangement^{1,2}

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Abstract: 1-Methylene-3-vinylcyclopentane (**3**) and 5-methylenecycloheptene (**4**) undergo first-order interconversion in the temperature range 260–300 °C with $\Delta H_{287}^{\ddagger} = 35.5 \pm 1.0$ kcal/mol for the reactions $3 \rightarrow 4$ and $4 \rightarrow 3$ and $\Delta S_{287}^{\ddagger} = -16.6 \pm 3.0$ eu for the reaction $3 \rightarrow 4$ and -12.7 ± 3.0 eu for the reaction $4 \rightarrow 3$. A study of the conversion of **4**, labeled with deuterium at the *exo*-methylene group, to **3**, labeled exclusively in the five-membered ring, establishes the reaction as a concerted [3,3]-sigmatropic process.

In an earlier study we reported the thermal conversion of 2-methyl-2-vinyl-5-methylenetetrahydrofuran (**1**) to 4-methyl-4-cycloheptenone (**2**).³ Although the unidirectional nature of the rearrangement and the characteristic activation quantities seemed to safely place the reaction in the category of concerted [3,3]-sigmatropic processes (an aliphatic Claisen rearrangement), a vestige of uncertainty remained. Conceivably, a diradical or a sequence of two [1,3]-sigmatropic shifts could have intervened and the single product observed was simply a result of thermodynamic control. Accordingly, we undertook a study of an analogous "Cope" system in which the thermodynamic bias for the formation of a carbonyl compound would be absent. In this paper we report on the Cope isomerization of 1-methylene-3-vinylcyclopentane (**3**) and 5-methylenecycloheptene (**4**).



Results

Preparation of 3 and 4. The requisite 1,5-dienes, **3** and **4**, were prepared as outlined in Schemes I and II. Dieckmann cyclization of diethyl β -vinyl adipate (**5**)⁴ produced a mixture of β -keto esters which upon hydrolysis and decarboxylation

Scheme I

