84649-43-4; *cis*-cr($O_9$), 82959-76-0; *cis*-cr($O_7$)Na complex, 84649-46-7; *cis*-cr($O_7$)K complex, 84649-47-8; *cis*-cr($O_7$)Rb complex, 84680-87-5; *cis*-cr($O_7$)Cs complex, 84649-48-9; *cis*-cr($O_8$)Na complex, 84649-49-0; *cis*-cr($O_8$)K complex, 84649-50-3; *cis*-cr($O_8$)Rb complex, 84649-51-4; *cis*-cr($O_8$)Cs complex, 84649-52-5; *cis*-cr($O_9$)Na complex, 84680-88-6; *cis*-cr($O_9$)K complex, 84680-89-7; *cis*-cr($O_9$)Rb complex, 84680-90-0; *cis*-cr($O_9$)Cs complex, 84680-91-1; *trans*-cr($O_7$), 84649-44-5; *trans*-cr($O_8$), 84649-45-6; *trans*-cr($O_9$), 82959-73-7.

---

# Temperature Dependence of the Photochemistry of Aryl Alkyl Ketones[1]

**M. V. Encina,[2] E. A. Lissi,*[2] Else Lemp,[2] A. Zanocco,[3] and J. C. Scaiano*[4]**

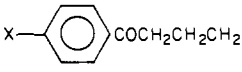
*Contribution from the Department of Chemistry, Facultad de Ciencias, Universidad de Santiago, Santiago, Chile, Departmento de Ciencias Formativas, Universidad de Chile, Santiago, Chile, and Division of Chemistry, National Research Council of Canada, Ottawa, Canada K1A 0R6.*

*Received May 7, 1982*

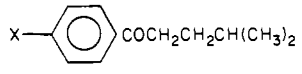
**Abstract:** The photochemistry of several phenyl alkyl and *p*-anisyl alkyl ketones has been examined using laser flash photolysis and conventional quantum yield techniques. The methoxy-substituted ketones show higher activation energies ($\Delta E_a \sim 3$ kcal mol$^{-1}$) for the Norrish type I and type II processes. It is concluded that both reactions are adiabatic processes occurring from the triplet $n\pi^*$ surface. In the case of *p*-methoxy-substituted ketones the upper $n\pi^*$ surface is reached from the low-lying $\pi\pi^*$ triplet, with the energy gap between both states reflected as an increase in the activation energy.

The photochemistry of alkyl and phenyl alkyl ketones has been extensively studied, and the main factors which determine the rate constants for the type I cleavage and type II intramolecular hydrogen abstraction are now well characterized.[5-18] In the case of phenyl alkyl ketones, their photobehavior for a given alkyl group is determined by the relative positions of the $n\pi^*$ and $\pi\pi^*$ excited states.[8,10,19-26] In particular, Wagner et al.[20,21] have carried out extensive studies of the effect of ring substituents on the type II photoreaction of aryl alkyl ketones in order to understand how interactions between nearby excited triplets affect chemical reactivity; they concluded that *p*-methoxy ketones react primarily from equilibrium concentrations of the higher $n\pi^*$ triplet state. Data on the type I cleavage of ketones with lower $\pi\pi^*$ excited triplets have been obtained only employing *p*-methoxyphenyl *tert*-butyl ketone at a single temperature.[9] The results obtained also suggest that the reaction takes place from the $n\pi^*$ triplet surface. In order to have a more complete understanding of the reactivity of $\pi\pi^*$ excited triplets, we have carried out a detailed study of the temperature dependence of the photochemistry of phenyl alkyl and *p*-anisyl alkyl ketones which react via both type I and type II photoprocesses. The measurements were carried out employing conventional steady-state and laser flash photolysis techniques.

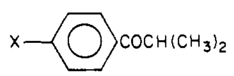
The ketones studied have the structures I–IV.



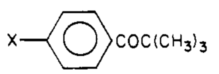
I



II



III



IV

a, X = H, b, X = $CH_3O$

## Results

**Ketones Which Undergo Intramolecular Hydrogen Abstraction.** The results can be interpreted in terms of the simplified mechanism, reactions 1–6, where K represents a ketone capable of undergoing the Norrish type II reaction.

$$K \xrightarrow{h\nu} \rightarrow {}^3K \tag{1}$$

$$ {}^3K \xrightarrow{k_{II}} \text{1,4-biradical} \tag{2}$$

$$ {}^3K \xrightarrow{k_d} K \text{ (or products)} \tag{3}$$

$$\text{1,4-biradical} \rightarrow \text{fragmentation} \tag{4}$$

$$\text{1,4-biradical} \rightarrow \text{cyclization} \tag{5}$$

$$\text{1,4-biradical} \rightarrow K \tag{6}$$

$k_d$ includes the interaction with the solvent and/or solvent impurities. Both the steady-state photolysis method and the direct detection of the triplet state have shortcomings when applied to these ketones. The kinetics of triplet decay are controlled by ($k_{II} + k_d$); thus an estimation of $k_d$ is required to obtain the value of $k_{II}$. Further, the presence of the relatively long-lived 1,4-biradical can interfere with the direct determination of the triplet lifetime. In those cases where the corresponding activation energies ($E_{II}$ and $E_d$) are substantially different, the first difficulty can be solved by working over an extended temperature range.

The second difficulty (biradical interference or too short a lifetime)[27] can be overcomed by using an indirect approach in the

---

(1) Issued as NRCC-20595.
(2) Universidad de Santiago.
(3) Universidad de Chile.
(4) National Research Council of Canada.
(5) Abuin, E.; Lissi, E. A. *J. Photochem.* **1976/77**, *6*, 1.
(6) Encina, M. V.; Lissi, E. A. *J. Photochem.* **1978**, *8*, 131.
(7) Encina, M. V.; Lissi, E. A.; Scaiano, J. C. *J. Phys. Chem.* **1980**, *84*, 948.
(8) Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168.
(9) Lewis, F. D.; Magyar, J. G. *J. Org. Chem.* **1972**, *37*, 2102.
(10) Scaiano, J. C.; Lissi, E. A.; Encina, M. V. *Rev. Chem. Intermed.* **1978**, *2*, 139.
(11) Wagner, P. J.; Kelso, P. A.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 7480.
(12) Wagner, P. J.; Kochevar, I. E.; Kemppainen, A. E. *J. Am. Chem. Soc.* **1972**, *94*, 7489.
(13) Wagner, P. J.; Kemppainen, A. E. *J. Am. Chem. Soc.* **1972**, *94*, 7495.
(14) Wagner, P. J.; Kelso, P. A.; Kemppainen, A. E.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 7500.
(15) Wagner, P. J.; Kelso, P. A.; Kemppainen, A. E.; McGrath, J. M.; Schott, H. N.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 7506.
(16) Lewis, F. D.; Johnson, R. W.; Johnson, D. E. *J. Am. Chem. Soc.* **1974**, *96*, 6090.
(17) Lewis, F. D.; Hilliard, T. A. *J. Am. Chem. Soc.* **1972**, *94*, 3852.
(18) Lewis, F. D. *J. Am. Chem. Soc.* **1970**, *92*, 5602.
(19) Naito, I.; Schnabel, W. *Z. Naturforsch. A* **1979**, *34*, 1251.
(20) Wagner, P. J.; Kemppainen, A. E.; Schott, H. N. *J. Am. Chem. Soc.* **1973**, *95*, 5604.
(21) Wagner, P. J.; Kemppainen, A. E.; Schott, H. N. *J. Am. Chem. Soc.* **1970**, *92*, 5280.
(22) Scaiano, J. C.; Selwyn, J. C. *Macromolecules* **1981**, *14*, 1723.
(23) Selwyn, J. C.; Scaiano, J. C. *Polymer* **1980**, *21*, 1365.
(24) Scaiano, J. C.; Stewart, L. C. *Polymer* **1982**, *23*, 913.
(25) Wagner, P. J.; Nakahira, T. *J. Am. Chem. Soc.* **1973**, *95*, 8474.
(26) Wagner, P. J.; Nakahira, T. *J. Am. Chem. Soc.* **1974**, *96*, 3668.

0002-7863/83/1505-1856$01.50/0

laser photolysis experiments. In this case the measurements can be carried out using a good triplet energy acceptor, which in turn yields an easily detectable triplet. We have used 1-methylnaphthalene, which has proved quite convenient in earlier studies.[27,28] The yield of triplet 1-methylnaphthalene ($\Phi_N$), measured by its optical absorption at 420 nm ($A_N$), follows a conventional Stern–Volmer type of dependence (eq 7) and yields $k_q\tau_T$ from the intercept-to-slope ratio:

$$1/\Phi_N = 1 + 1/k_q\tau_T[\mathrm{N}] \tag{7a}$$

$$1/A_N = a + a/k_q\tau_T[\mathrm{N}] \tag{7b}$$

where $a$ is a proportionality constant.

A wide range of $k_q$ values has recently been measured in this laboratory over an extended range of temperatures,[29] and in various solvents, it is thus possible to derive "absolute" $\tau_T$ values from the $k_q\tau_T$ values obtained using eq 7. The values of $\tau_T$ are then related to $k_{\mathrm{II}}$ and $k_d$ according to

$$\tau_T^{-1} = k_{\mathrm{II}} + k_d \tag{8}$$

Thus, in order to obtain $k_{\mathrm{II}}$ values it becomes necessary to measure $k_d$, or its ratio with $k_{\mathrm{II}}$. The photoelimination quantum yield is given by:

$$\Phi_{\mathrm{II}} = P_{\mathrm{II}}k_{\mathrm{II}}/(k_{\mathrm{II}} + k_d) \tag{9}$$

$$P_{\mathrm{II}} = k_4/(k_4 + k_5 + k_6) \tag{10}$$

Since $P_{\mathrm{II}}$ cannot be directly evaluated, the usual procedure involves working under (or making a direct comparison with) conditions such that $P_{\mathrm{II}} \sim 1$. This was achieved by adding 1.2 M pyridine to the solvents.[8] In 1.2 M pyridine in *n*-hexane, $\Phi_{\mathrm{II}}$ in the photolysis of IIa and IIb was practically 1 from 296 to 370 K. Further, this concentration of pyridine did not modify appreciably the triplet lifetime of IIb, showing that it does not quench the triplets and that it does not modify substantially the reactivity of the triplet by increasing the $n\pi^*-\pi\pi^*$ energy gap.

**1. *p*-Methoxyisocaprophenone (IIb).** Steady-state quenching experiments in *n*-hexane solutions employing naphthalene as quencher were carried out between 296 and 370 K, allowing evaluations of $k_q\tau_T$. Since $k_{\mathrm{II}} \gg k_d$ ($\Phi_{\mathrm{II}} \gg 0.9$ over all the temperature range), an Arrhenius plot of the $k_q\tau_T$ values (shown in Figure 1) leads to: $\log (k_q\tau_T) = (0.49 \pm 0.49) + (3.63 \pm 0.74)/2.3RT$ (with $RT$ in kcal/mol). If we take $\log k_q = 11.1 - 1.9/2.3RT$,[29] we obtain

$$\log k_{\mathrm{II}} = 10.6 - 5.5/2.3RT$$

**2. Isocaprophenone (IIa).** For this ketone it can be safely assumed that $k_{\mathrm{II}} \gg k_d$.[30] The triplet decay could not be monitored directly because of biradical interference and the short triplet lifetime.[30,31] The triplet lifetime was then evaluated from the 1-methylnaphthalene triplet yield as a function of the 1-methylnaphthalene concentration as described above. The values of $k_q\tau_T$ obtained in the temperature range 341 to 246 K are plotted against the inverse temperature in Figure 1. These data lead to $\log k_q\tau_T = (0.84 \pm 0.07) + (0.84 \pm 0.10)/2.3RT$, which, combined with the proper quenching data leads to

$$\log k_{\mathrm{II}} = 10.3 - 2.7/2.3RT$$

in isooctane as solvent. Grotewold et al.[30] obtained, from steady-state experiments:

$$\log (k_q/k_{\mathrm{II}}) = -0.1 + 1.6/2.3RT$$

in benzene employing *cis*-1,3-pentadiene as quencher. Combining these data with $k_q$ values measured in closely related systems[29] leads to:

$$\log k_{\mathrm{II}} = 10.9 - 3.02/2.3RT$$

in good agreement with the present results.

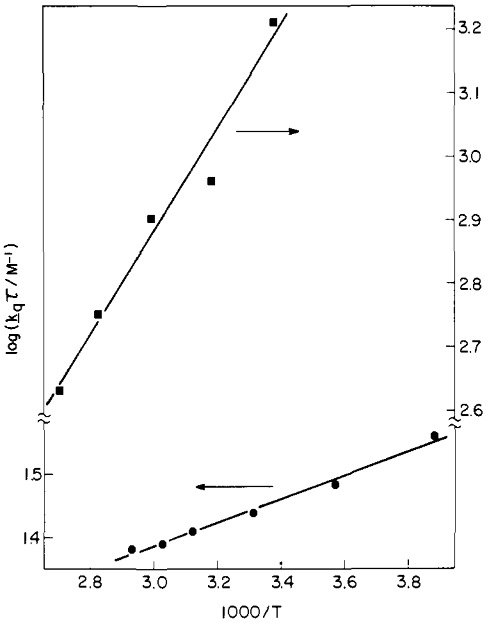


**Figure 1.** Arrhenius plots showing the temperature dependence of $k_q\tau_T$ for IIb in *n*-hexane (■) and IIa in isooctane (●).

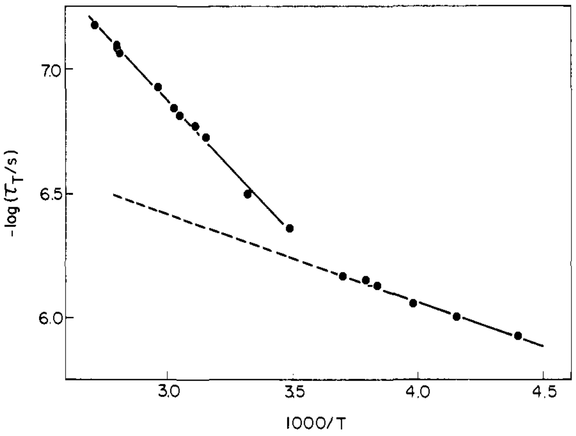


**Figure 2.** Temperature dependence of the triplet lifetime for Ib in isooctane.

**3. *p*-Methoxyvalerophenone (Ib).** For this ketone the triplet decay can be measured directly by its absorption at 380 nm. The decay traces follow first-order kinetics. The values of $\tau_T^{-1}$ obtained, plotted against the inverse temperature, are given in Figure 2. This plot shows regions with two different slopes, one at low and the other at high temperature. Since $\tau_T^{-1} = k_{\mathrm{II}} + k_d$, this behavior can be explained in terms of the predominance of $k_d$ at low temperatures and an increased relevance of $k_{\mathrm{II}}$ at higher temperatures. The contribution of $k_d$ at high temperatures was evaluated by extrapolation of the low-temperature data, thus allowing (by subtraction) an evaluation of $k_{\mathrm{II}}$. Plotting the $k_{\mathrm{II}}$ values obtained in isooctane against the inverse temperature gives a good linear relationship:

$$\log k_{\mathrm{II}} = 11.2 - 6.9/2.3RT$$

The value at 298 K obtained with this relationship ($1.5 \times 10^6$ s$^{-1}$) is nearly three times larger than that reported by Wagner et al.[20] in benzene solution.

**4. Valerophenone (Ia).** Direct measurement of the triplet decay was perturbed by biradical interference even at low temperature.

---

(27) A discussion of this problem has been published: Bays, J. P.; Encinas, M. V.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 727.

(28) Bays, J. P.; Encinas, M. V.; Scaiano, J. C. *Macromolecules* **1980**, *13*, 815.

(29) Scaiano, J. C.; Leigh, W. J., to be submitted for publication.

(30) Grotewold, J.; Soria, D.; Previtali, C. M.; Scaiano, J. C. *J. Photochem.* **1972/73**, *1*, 471.

(31) Small, R. D., Jr.; Scaiano, J. C. *J. Phys. Chem.* **1977**, *81*, 2126.

Table I. Kinetic Data for Intramolecular Hydrogen Abstraction (Norrish Type II Process)

| substrate | solvent | method | $k_{II}/s^{-1}$ (298 K) | log ($A/s^{-1}$) | $E_{II}^{a}$ |
|---|---|---|---|---|---|
| Ia | benzene | quenching$^{b}$ | $1.8 \times 10^{8}$ | 11.2 | 4.0 |
| Ib | isooctane | triplet decay | $1.3 \times 10^{6}$ | 11.2 | 6.9 |
| IIa | benzene | quenching$^{b}$ | $4.9 \times 10^{8}$ | 10.9 | 3.0 |
| | isooctane | naphthalene$^{c}$ | $4.9 \times 10^{8}$ | 10.3 | 2.7 |
| IIb | *n*-hexane | quenching | $9.5 \times 10^{6}$ | 10.6 | 5.5 |

[a] In kcal mol$^{-1}$. [b] Based on data from ref 30, using *cis*-1,3-pentadiene as quencher. [c] Monitoring the formation of triplet naphthalene at 420 nm.

The values of $k_{II}$ were then obtained by combining the $k_q\tau_T$ values reported by Grotewold et al.[30] and recent evaluations of $k_q$ as a function of temperature.[29] By this method we obtained:

$$\log k_{II} = 11.15 - 4.0/2.3RT$$

The data obtained for internal hydrogen abstraction in nonpolar solvents are summarized in Table I.

**5. Solvent Effects.** The effect of the solvent was evaluated at 333 K employing *n*-hexane and ethanol as solvents by measuring $k_q\tau_T$ values for IIa and IIb. If it is assumed that similar $k_q$ values apply for both ketones in a given solvent, the relationship between the slopes of the Stern–Volmer plots directly provides $(k_{II})_{IIb}/(k_{II})_{IIa}$. The values obtained in *n*-hexane and ethanol were 0.048 and 0.0043, respectively. If it is assumed that $k_q$ in ethanol is nearly one-half $k_q$ in *n*-hexane, we obtain $(k_{II})_{ethanol}/(k_{II})_{hexane} \sim$ 1 and 0.076 for IIa and IIb, respectively.

**Ketones Which React by α-Bond Cleavage.** These ketones have the disadvantage that they have to be photolyzed at rather high temperatures because the type I process is relatively minor. Further, in order to obtain the photocleavage yield from a product analysis, it is necessary to quantitatively trap all free radicals produced and to estimate the amount of cage recombination. The experiments were carried out in the presence of hexanethiol to trap the alkyl radicals produced.[17,32] In experiments carried out under conditions such that the thiol traps all the radicals but does not quench the excited triplets, the mechanism of reactions 11–16 would apply:

$$K \xrightarrow{h\nu} \rightarrow {}^3K \qquad (11)$$

$${}^3K \rightarrow (Ar\dot{C}O + R\cdot) \qquad (12)$$

$${}^3K \rightarrow K \qquad (13)$$

$$(Ar\dot{C}O + R\cdot) \rightarrow K \qquad (14)$$

$$(Ar\dot{C}O + R\cdot) \rightarrow Ar\dot{C}O + R\cdot \qquad (15)$$

$$R\cdot + R'SH \rightarrow RH + R'S\cdot \qquad (16)$$

and

$$\Phi_I = \Phi_{RH}/(1 - \alpha) \qquad (17)$$

where α is given by the probability of cage recombination. That the thiol was playing the desired role was shown by the independence of $\Phi_{RH}$ upon the thiol concentration, in the concentration range used. The amount of cage recombination at each temperature was evaluated by the method previously described[32] and assuming $\alpha = 0.3$ at 298 K. In any case, the error introduced by an improper evaluation of α is not enough to modify appreciably the kinetic data derived.

The mechanism of reactions 11–16 leads to:

$$k_d/k_I = \Phi_I^{-1} - 1 \qquad (18)$$

and

$$\tau_T^{-1} = k_I + k_d \qquad (19)$$

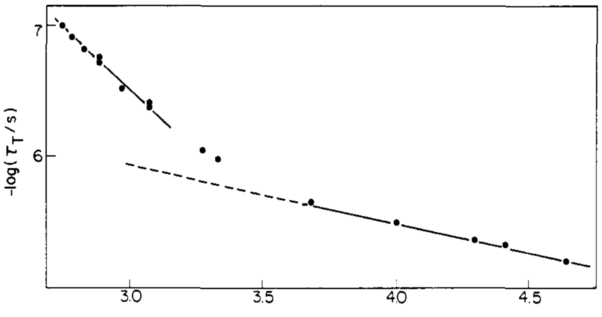


Figure 3. Temperature dependence of the triplet lifetime for IVb in *n*-hexane.

**1. *p*-Methoxyphenyl *tert*-Butyl Ketone (IVb).** The decay of the triplet can be directly measured at 380 nm. Good first-order decays were obtained between 223 and 363 K. The values of $\tau_T^{-1}$ plotted against the inverse temperature show a clear change in slope (see Figure 3) that can be attributed to the predominance of $k_d$ at low temperatures and an increased contribution of $k_I$ at the higher temperatures. Subtraction of $k_d$ values obtained by extrapolation of the low-temperature data leads to values of $k_I$. These values can be represented by:

$$\log k_I = 12.8 - 9.96/2.3RT$$

in *n*-hexane as solvent. A similar treatment of the data obtained in acetonitrile and methanol gives $\log k_I = 13.6 - 11.5/2.3RT$ and $\log k_I = 13.2 - 11.4/2.3RT$, respectively.

The values of $\Phi_I$ increase from 0.3 to 0.89 when the temperature increases from 283 to 363 K, as required by our interpretation of the data of Figure 3. A value of $\Phi_I$ (not corrected by cage recombination) of 0.174 has been reported by Lewis and Magyar[9] in benzene at room temperature. A plot of $\log(\Phi_I^{-1} - 1)$ against $T^{-1}$ is given in Figure 4. In this figure we have also included $k_d/k_I$ values from the triplet decay; both sets of data agree well and lead to $(E_I - E_d) = 7.8$ kcal mol$^{-1}$. Since from the low-temperature data $E_d$ can be taken as 2.0 kcal mol$^{-1}$, we obtain $E_I = 9.8$ kcal mol$^{-1}$.

An independent estimate of $k_I$ (and $E_I$) can be obtained from quenching experiments, since

$$k_I = k_q\Phi_I/(k_q\tau_T) \qquad (20)$$

In order to obtain reproducible results in quenching experiments, the conversion has to be kept extremely low. Under these conditions $(k_q\tau_T)$ at 293 K in *n*-hexane with 1-methylnaphthalene as quencher was 4600 M$^{-1}$. A value of 7360 M$^{-1}$ has been reported by Lewis and Magyar in benzene employing naphthalene as quencher.[9] Arrhenius treatment of the $k_I$ values obtained with eq 20 gives:

$$\log k_I = 13.3 - 10.0/2.3RT$$

in good agreement with the values given above and in Table II.

**2. Phenyl *tert*-Butyl Ketone (IVa).** The $\Phi_I$ values for this ketone are, at a given temperature, larger than those of IVb (i.e., 0.44 at 283 K and 0.9 at 363 K). For this ketone in benzene Lewis and Magyar[9] have reported values of $\Phi_I = 0.3$ and $k_q\tau_T = 447$ M$^{-1}$ at room temperature. Plotting the values of $k_I$ obtained with eq 20 as a function of temperature leads to:

$$\log k_I = 12.3 - 7.3/2.3RT$$

**3. *p*-Methoxyphenyl Isopropyl Ketone (IIIb).** At room temperature the type I cleavage of this ketone is very small. The experiments were then carried out at temperatures higher than 369 K in dodecane as solvent. At this temperature $\Phi_I$ was only 0.009. The value increases to 0.19 at 453 K. In agreement with the low contribution of the type I cleavage to the triplet deactivation up to 369 K, the laser photolysis data showed a behavior consistent with a single decay process from 218 to 353 K with an activation energy of ca. 2.0 kcal mol$^{-1}$ that can be attributed to reaction 13.

---

(32) (a) Encina, M. V.; Nogales, A.; Lissi, E. A. *J. Photochem.* **1975**, *4*, 75. (b) Wagner, P. J.; McGrath, J. M. *J. Am. Chem. Soc.* **1972**, *94*, 3849.

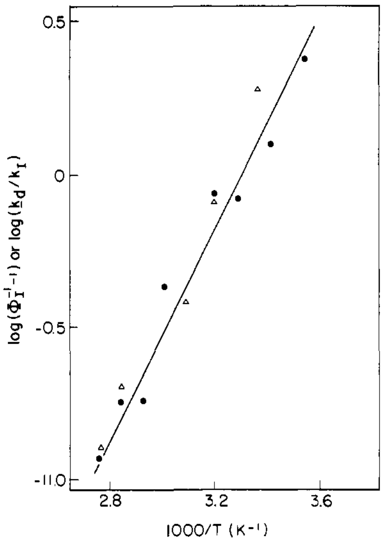


**Figure 4.** Temperature dependence of ($\Phi_I^{-1} - 1$) (●) and of $k_d/k_I$ values (▵) derived from laser experiments for IVb in *n*-hexane.

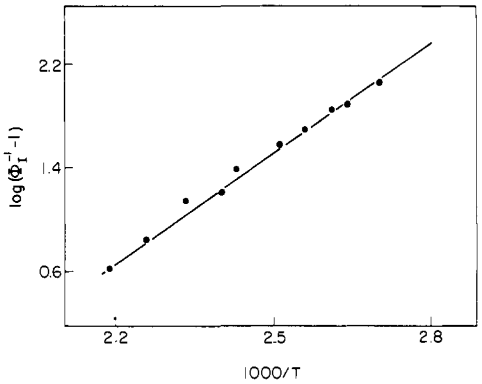


**Figure 5.** Temperature dependence of ($\Phi_I^{-1} - 1$) for IIIb in dodecane.

Table II. Kinetic Data for the Norrish Type I Reaction

| sub-strate | solvent | method | $k_I$/s$^{-1}$ (298 K) | log ($A$/s$^{-1}$) | $E_I$ |
|---|---|---|---|---|---|
| IVb | *n*-hexane | triplet decay | $2.94 \times 10^5$ | 12.8 | 9.96 |
|  | acetonitrile | triplet decay | $1.37 \times 10^5$ | 13.6 | 11.5 |
|  | methanol | triplet decay | $6.44 \times 10^4$ | 13.2 | 11.4 |
| IVa | *n*-hexane | eq 20 | $8.45 \times 10^6$ | 12.3 | 7.3 |
| IIIb | dodecane | eq 18 | 68.1 | 12.8 | 14.9 |
| IIIa | dodecane | quenching | $7.4 \times 10^3$ | 12.7 | 12.0 |

Figure 5 shows a plot of log ($\Phi_I^{-1} - 1$) against inverse temperature. From these data and we obtain

$$\log (k_d/k_I) = -(5.45 \pm 0.62) + (12.8 \pm 1.2)/2.3RT$$

which, combined with the laser data at lower temperature, yields $\log k_I = 12.8 - 14.9/2.3RT$.

**4. Phenyl Isopropyl Ketone (IIIa).** As in the case of the *tert*-butyl ketones, photocleavage quantum yields are considerably larger in the unsubstituted than in the *p*-methoxy-substituted ketone. The values of $\Phi_I$ in dodecane increased from 0.1 at 369 to 0.32 at 453 K. Combining $k_q\tau_T$ and $\Phi_I$ values leads to:

$$\log k_I = 12.7 - 12/2.3RT$$

**5. Solvent Effects.** The effect of solvent associated with *p*-methoxy substitution was evaluated by measuring $k_q\tau_T$ and $\Phi_I$ in *n*-hexane and ethanol for IVa and IVb. Assuming that $k_q$ in a given solvent is the same for both ketones, it was obtained that at 333 K $(k_I)_{IVa}/(k_I)_{IVb}$ values were 3.0 and 33.0 in *n*-hexane and ethanol, respectively. Furthermore, if it is assumed that at 333 K $(k_q)_{n\text{-hexane}}$ is nearly two times $(k_q)_{\text{ethanol}}$, we obtain $(k_I)_{\text{ethanol}}/(k_I)_{n\text{-hexane}} \sim 1$ for IVa and 0.1 for IVb.

## Discussion

It is important to note that in all cases where it is possible to compare directly kinetic data obtained using direct detection or quenching techniques the agreement is quite good. This is to a considerable extent the result of the use of absolute kinetic data for the quenching processes.[29] The agreement obtained provides support for the assumptions used and shows that one can confidently compare data obtained using different methods.

The lower reactivity of methoxy-substituted ketones is due, almost exclusively, to an increase in activation energy for both the Norrish type I and type II processes. Extensive changes in entropic factors do not seem to be involved. In the case of intramolecular hydrogen abstraction, this type of behavior had been assumed by Wagner et al.[20,21] in their interpretation of substituent effects and is fully consistent with the activation energy difference observed in the case of 1-benzoyl-4-*p*-anisoylbutane.[25] A similar finding was reported by Steel et al.[33] in their study of intermolecular hydrogen abstraction. These observations are also consistent with studies in polymer systems,[22-24] where it has been shown that the activation energy for triplet decay in polymers containing *p*-methoxyacrylophenone units is about 3 kcal mol$^{-1}$ higher than in the case of phenyl vinyl ketone units.

The magnitude of the activation energies and $A$ factors measured suggest that the reactions are simple adiabatic processes that can be interpreted in terms of transition state reaction rate theory. The $A$ factors for the type I process of around $10^{13}$ s$^{-1}$ suggest a transition configuration strongly resembling the precursor triplet state, in contrast to the thermal bond cleavages where the transition state approaches the radical products and thus leads to higher preexponential factors. The results clearly do not support Formosinho's interpretation of the process in terms of a tunneling mechanism;[34] in our view, these results are sufficiently conclusive, that Formosinho's mechanism can be ruled out.

The larger energy barrier found for the ketones with low-lying $\pi\pi^*$ states contrasts with Salem's[35] correlation diagrams that imply a more favorable type I process for $\pi\pi^*$ states.

The magnitude of the activation energies for the type I process of $n\pi^*$ triplets seems consistent with the few values that have been reported in the past. Thus acetophenone in the gas-phase loses a methyl radical with $E_a \sim 20$ kcal mol$^{-1}$,[36] 4-methyl-2-pentanone cleaves with $E_a = 14.4$ kcal mol$^{-1}$ (hexane solvent),[6] while the secondary and tertiary sites studied in this work have activation energies of 12 and 10 kcal mol$^{-1}$, respectively (see Table II).

A crucial point that deserves attention is the fact that the activation energy difference associated with *p*-methoxy substitution is essentially insensitive to the actual mode of reaction (type I or type II) as well as to the details of the substitution at the alkyl group. This type of similarity, observed in the analysis of rate constants for the type II process, led Wagner et al.[20] to propose that the reaction arises from the thermally populated $n\pi^*$ state. The data presented herein not only support Wagner's proposal but, by showing that the same ideas apply to the type I process, make any mechanism requiring reaction from a different electronic state highly unlikely. That is, two completely different triplet state reactions are not likely to show, upon *p*-methoxy substitution, the same difference in activation energy and selectivity, and virtually no change in $A$ factor unless they are actually taking place from the same electronic state. Thus, in terms of a simplified potential energy surface, the reaction can be viewed as taking place from a thermally equilibrated upper $T_2$ ($n\pi^*$) state, or, alternatively, the lower $T_1$ ($\pi\pi^*$) state can "search" the surface with the actual crossing or "equilibration" taking place along the reaction coordinate. In either case, the activation energy measured from the low-lying triplet, $T_1$, will be given by:

$$(E_a)_{T_1} = (E_a)_{T_2} + (E_{T_2} - E_{T_1}) \tag{21}$$

where the term $(E_{T_2} - E_{T_1})$ is simply the energy gap between the

---

(33) Berger, M.; McAlpine, E.; Steel, C. *J. Am. Chem. Soc.* **1978**, *100*, 5147.

(34) Formosinho, S. J. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 1313.

(35) Salem, L. *J. Am. Chem. Soc.* **1974**, *96*, 3486.

(36) Rennert, A. R.; Steel, C. *Chem. Phys. Lett.* **1981**, *78*, 36–39.

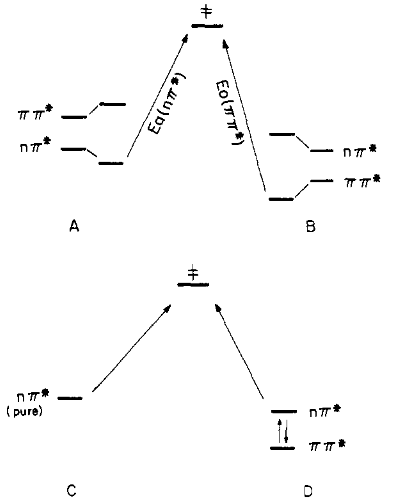


**Figure 6.** Effect of "mixing" and substituent effects on the experimental activation energies.

two triplet levels. The value of $(E_a)_{T_2}$ can differ from that of the unsubstituted ketone owing to both a "substituent effect" as well as the mixed character of the second triplet level, $T_2$. The influence of the substituent upon the reactivity of the $n\pi^*$ state was inferred by Wagner et al. (in the type II process)[20] by examining the effect of substituents upon the reactivity of $n\pi^*$ states with near-$\pi\pi^*$ excited states lying above them. The extrapolation of these results to ketones with lower $\pi\pi^*$ states may not be straightforward because of the mixed character of the states.[33] However, according to Wagner[37] vibronic mixing is significant only when the $n\pi^*$ and $\pi\pi^*$ levels are within 1 kcal mol$^{-1}$ of each other.

A different approach has been followed by Steel et al.[33] who assume that substituent effects arise from a different degree of mixing. Figure 6 (A and B) illustrates the effect mixing would have on the activation parameters, while the bottom part of the figure (C and D) illustrates Wagner's approach assuming that substituent effects predominate. These effects have been estimated to account for a factor of 2 in the type II process.[20] Thus, since our average difference in activation energy is about 2.8 kcal mol$^{-1}$, and allowing for a factor of 2, we have:

$$2.4 \le (E_{T_2} - E_{T_1}) \le 3.2 \text{ kcal mol}^{-1}$$

for the *p*-methoxy ketones in nonpolar solvents. These differences are very similar to those estimated by Wagner et al.[20] The effects of substituents upon the type I reaction have not been evaluated, but our data indicate that they must be of a magnitude similar to that observed for the intramolecular hydrogen abstraction.

The effect of the solvent is rather difficult to quantify owing to the influence that it can have on both the relative energies of the states and the reactivity of the "pure" $n\pi^*$ state.[7] First, we note that for both type I and type II processes $(k)_{\text{ethanol}}$ is very similar to $(k)_{\text{hexane}}$ for the unsubstituted ketones. Since the reactivity of a pure $n\pi^*$ state could be expected to be larger in the more polar solvent,[6] this effect must be compensated by mixing with the almost isoelectronic $\pi\pi^*$ state (and/or by a decrease in the population of the almost "pure" $n\pi^*$ state). The relationship between the rates of reaction of the *p*-methoxy-substituted and unsubstituted ketones in ethanol and in *n*-hexane indicates that the selectivity is approximately 10 times larger in ethanol. If this is an activation energy effect, it would amount to nearly 1.5 kcal mol$^{-1}$. The experimentally determined difference in activation energies for the *p*-methoxyphenyl *tert*-butyl ketone in *n*-hexane and methanol was 1.4 kcal mol$^{-1}$, in very good agreement with the value estimated from quenching experiments. The activation energy difference between the *p*-methoxy-substituted and the unsubstituted ketone in ethanol is then approximately 4.4 kcal mol$^{-1}$ for both the type I and type II processes. This result is also compatible with a common mechanism for both reactions, namely, crossing to the upper $n\pi^*$ surface prior to the critical configuration.

## Experimental Section

**Materials.** *p*-Methoxyphenyl *tert*-butyl ketone (IVb) was prepared by the Friedel–Crafts method, by reaction of 17.3 g of anisole, 16 g of $AlCl_3$, and 9.65 g of pivaloyl chloride in 100 mL of petroleum ether at 0 °C (80% yield; bp 128–130 °C (7 torr)). *p*-Methoxyphenyl isopropyl ketone (IIIb) was prepared by the same technique, from anisole and isobutanoyl chloride (84% yield, bp 134 °C (12 torr)).

*p*-Methoxyphenyl-4-methylvalerophenone (IIb) was prepared by oxidation of 12.3 g of 1-*p*-methoxyphenyl-4-methyl-1-pentanol with 30 g of $CrO_3$:(pyridine)$_2$ complex in dichloromethane (68% yield, bp 136–137 °C (5 torr)).

Phenyl *tert*-butyl ketone (IVa) was prepared by addition of 50 mL of phenylmagnesium bromide (2 M in $CH_2Cl_2$) to 7.6 g of pivaloyl chloride in 25 mL of $CH_2Cl_2$ at 0 °C (71% yield, bp 70–72 °C (1 torr)).

The ketones prepared by the synthetic procedures given above all gave good elemental analyses and were characterized by NMR; their purity was verified by gas chromatography. All other ketones were purchased from Aldrich and were distilled under vacuum.

**Quantum Yields.** Photolyses were carried out in a merry-go-round apparatus employing light at 366 nm. Experiments at temperatures over 100 °C were carried out in a modified apparatus heated by boiling liquids. Product analyses were carried out at low conversions using samples degassed by several freeze–pump–thaw cycles. Valerophenone was used as an actinometer, taking the quantum yield of acetophenone formation as 0.30 in benzene at room temperature.

**Laser Flash Photolysis.** The samples (usually 1 mL) were contained in Suprasil cells made of rectangular tubing (3 × 7 mm$^2$). The pulses (337.1 nm, ~8 ns, up to 10 mJ) from a Molectron UV-24 nitrogen laser were used for excitation. Our system has been fully interfaced with a PDP-11/23 computer that controls the experiment and provides suitable data gathering, processing, storage, and hardcopy facilities. Further details have been given elsewhere.[38]

**Acknowledgment.** Thanks are due to Mr. S. E. Sugamori for technical assistance. M.V.E. and E.A.L. thank NRCC for the support received under their guest scientist program.

**Registry No.** Ia, 1009-14-9; Ib, 1671-76-7; IIa, 2050-07-9; IIb, 21550-01-6; IIIA, 611-70-1; IIIb, 2040-20-2; IVa, 938-16-9; IVb, 2040-26-8.

---

(37) Wagner, P. J. *Top. Curr. Chem.* **1976**, *66*, 1–52.

(38) Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747.