

# End-to-End Cyclization of Hydrocarbon Chains: Temperature Effects on an Intramolecular Phosphorescence Quenching Reaction in Solution

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Received December 6, 1984

**Abstract:** Details are presented for kinetic studies of intramolecular and bimolecular phosphorescence quenching of a series of  $\omega$ -alkenyl esters of 4-benzoylbenzoic acid [**O-n**; benzophenone-4-CO<sub>2</sub>(CH<sub>2</sub>)<sub>n</sub>CH=CH<sub>2</sub>]. Experiments are described for **O-n** ( $n = 1-21$ ) in two solvents, carbon tetrachloride and acetic acid, at a series of temperatures between -20 and 100 °C. Rate constants  $k_0(n)$  at 25 °C for intramolecular quenching by the CH=CH<sub>2</sub> group vary between  $2.7-28.2 \times 10^4 \text{ s}^{-1}$  in carbon tetrachloride and  $2.4-8.2 \times 10^5 \text{ s}^{-1}$  in acetic acid, varying sensitively with chain length. Activation energies in each solvent were independent of  $n$  (except for  $n = 8$  in CCl<sub>4</sub>), with  $E_a = 2.5 \text{ kcal/mol}$  in carbon tetrachloride and  $2.3 \text{ kcal/mol}$  in acetic acid. The chain length dependence of  $k_0(n)$  and the values of  $E_a$  are discussed in terms of the conformational properties of the hydrocarbon chain connecting the ketone and the quencher.

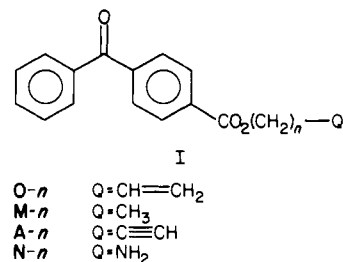
This manuscript reports the results of intramolecular phosphorescence quenching studies of a series of molecules **O-n** of the form benzophenone-4-CO<sub>2</sub>(CH<sub>2</sub>)<sub>n</sub>CH=CH<sub>2</sub>. These experiments are directed at understanding the conformational properties of oligomeric polymethylene chains. In addition, they contribute to our research group's overall objective of developing methods based upon luminescence spectroscopy for studying the conformation and dynamics of polymers.

While there are many kinds of experiments that can yield information about chain conformations,<sup>1,2</sup> intramolecular chemical reactions can provide information directly about chain cyclization probability.<sup>3</sup> The cyclized forms represent only a small subset of the total ensemble of conformations available to the chain. Their study permits one to examine whether factors such as steric effects (excluded volume) and solvent effects play a more important role in chain cyclization than they do in determining other chain properties, as for example,  $\langle r^2 \rangle$  the mean-squared end-to-end distance of the chain.

**Choice of Probe.** Our photochemical probe system may be represented pictorially as shown below. The specific requirements of the probe are as follows: (a) the cyclization reaction must yield an observable result; (b) the reaction site must be removed from the chain origin to minimize ring strain; (c) the chains must reach conformational equilibrium before reaction; (d) the chromophore must be long-lived; (e) the intramolecular reaction must occur on only a small fraction of encounters between the reactive site and the chain; (f) the chain length dependence of the reaction kinetics must be determinable; and (g) the probe must have conformational properties which can be simulated in terms of the rotational isomeric state model.

Benzophenone derivatives such as I are an ideal choice. They phosphoresce with lifetimes in the 1-250  $\mu\text{s}$  range. The excited triplet state can react with a variety of quenchers<sup>4,5</sup> (e.g., amines,

alkanes, alkenes, alkynes). These shorten the triplet lifetime, providing experimental means for studying cyclization kinetics.



Hydrocarbon chains in solution reach conformational equilibrium in tens of nanoseconds.<sup>6</sup> An appropriate quencher can be chosen which reacts with such a low efficiency that only 0.1% of the encounters between the reactants result in a chemical reaction. A pre-equilibrium is established prior to reaction. Luminescence quenching is the observable that can provide information of interest to the photochemist. For this purpose we examine here the case of Q = CH=CH<sub>2</sub>, molecules denoted as **O-n**. The corresponding methyl ester is denoted as **M-0**. Preliminary results for experiments at room temperature have previously been published.<sup>6</sup>

The choice of the ester **O-n** as our probe has another consequence. The quenching of aryl ketone phosphorescence by electron donors occurs through the formation of an electronically excited charge-transfer complex or exciplex intermediate.<sup>7-16</sup> It has been

(4) N. J. Turro, "Modern Molecular Photochemistry"; Benjamin/Cummings, Menlo Park, 1978.

(5) (a) M. V. Encina and E. A. Lissi, *J. Photochem.*, **6**, 173 (1976). (b) P. G. Wagner, *Top. Curr. Chem.*, **66**, 1 (1976). (c) J. C. Scaiano, *J. Photochem.*, **2**, 81 (1973). (d) R. O. Loutfy, R. Yip, and S. K. Dogra, *Tetrahedron Lett.*, 2843 (1977). (e) N. J. Turro and C. G. Lee, *Mol. Photochem.*, **4**, 427 (1972). (f) L. E. Friedrich and J. D. Bower, *J. Am. Chem. Soc.*, **95**, 6869 (1973).

(6) (a) A. Mar and M. A. Winnik, *Chem. Phys. Lett.*, **77**, 73 (1981). (b) A. Mar, S. J. Fraser, and M. A. Winnik, *J. Am. Chem. Soc.*, **103**, 4941 (1981).

(7) I. H. Kochevar and P. J. Wagner, *J. Am. Chem. Soc.*, **92**, 5742 (1970); **94**, 3859 (1972).

(8) (a) R. A. Caldwell, G. W. Sovocool, and R. P. Gajewski, *J. Am. Chem. Soc.*, **95**, 2549 (1973). (b) R. A. Caldwell, *J. Am. Chem. Soc.*, **92**, 1439 (1970).

(9) N. E. Schore and N. J. Turro, *J. Am. Chem. Soc.*, **97**, 2482 (1975). (10) R. O. Loutfy, S. K. Dogra, and R. W. Yip, *Can. J. Chem.*, **57**, 342 (1979).

(11) N. C. Yang, M. H. Hui, D. M. Shold, N. J. Turro, R. R. Hautala, K. Dawes, and J. C. Dalton, *J. Am. Chem. Soc.*, **99**, 3023 (1977).

(12) N. J. Turro, J. C. Dalton, G. Farrington, M. Niemczyk, and D. M. Pond, *J. Am. Chem. Soc.*, **92**, 6978 (1970).

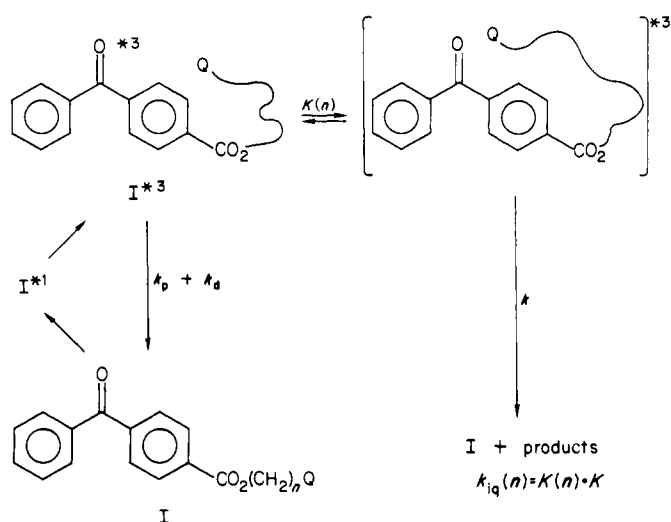
(13) M. A. Winnik and C. K. Hsiao, *Chem. Phys. Lett.*, **33**, 518 (1975).

(1) (a) P. J. Flory, "Statistical Mechanics of Chain Molecules", Wiley Interscience, New York, 1969. (b) D. Y. Yoon and P. J. Flory, *J. Chem. Phys.*, **61**, 5366 (1974).

(2) (a) G. W. Brady, *Acc. Chem. Res.*, **7**, 174 (1974). (b) G. D. Patterson, C. P. Lindsey, and G. R. Alms, *J. Chem. Phys.*, **69**, 3250 (1978). (c) M. Dettnermaier, *J. Chem. Phys.*, **68**, 2319 (1978). (d) Tancrede, P. Bothorel, P. de St. Romain, and D. Patterson, *J. Chem. Soc., Faraday Trans. 2*, **73**, 15 (1977). (e) G. D. Patterson and P. J. Flory, *J. Chem. Soc., Faraday Trans. 2*, **68**, 1098 (1972). (f) G. W. Brady and D. B. Fein, *J. Appl. Crystallogr.*, **8**, 261 (1975). (g) P. Tancrede, P. Bothorel, and D. Patterson, *J. Chem. Soc., Faraday Trans. 2*, **73**, 29 (1977).

(3) (a) M. Sisido, *Macromolecules*, **4**, 737 (1971). (b) P. J. Flory, U. W. Sutter, and M. Mutter, *J. Am. Chem. Soc.*, **98**, 5733 (1976). (c) P. J. Flory and J. A. Semlyen, *J. Am. Chem. Soc.*, **88**, 3209 (1966). (d) M. A. D. Fluendy, *Trans. Faraday Soc.*, **59**, 1681 (1963). (e) M. Lal and D. Spencer, *Mol. Phys.*, **22**, 649 (1971). (f) M. A. Winnik, D. Rigby, R. F. T. Stepto, and B. Lemaire, *Macromolecules*, **13**, 699 (1980).

Scheme I



suggested<sup>13,16</sup> that a specific geometry is required for effective quenching. The alkane chain imposes constraints on the orientations available between the quencher and the excited chromophore. The variation of the rate of intramolecular quenching as a function of chain length allows us to examine aspects of the specific geometry required for the quenching process.

**Choice of the Solvent.** Two classes of criteria apply in the choice of solvent. One involves the experimental aspect and the other the theoretical aspect of the study. Experimentally, the solvents selected must be inert or have a slow rate of reaction with the triplet state of benzophenone. One must be able to obtain them in sufficient purity to observe ketone phosphorescence emission in solution at room temperature.

Theoretically, we wished to compare the behavior of our probe in a polar and a nonpolar solvent. The solvents chosen were carbon tetrachloride and acetic acid. Although acetic acid has a low dielectric constant ( $\epsilon = 6$ ), it is protic; and since it is a fairly poor solvent for alkanes, reactivity differences in the two solvents might be expected. The  $n-\pi^*$  absorbance maximum of the methyl ester of benzophenone-4-carboxylic acid **M-0** is blue shifted<sup>16</sup> in acetic acid (341 nm) relative to that in carbon tetrachloride (346 nm). However, **M-0** has lowest  $n-\pi^*$  triplet states in both solvents and more importantly its triplet energy,  $E_T$ , in acetic acid (65.9 kcal/mol) and carbon tetrachloride (66.1 kcal/mol) are virtually identical.<sup>17</sup> Therefore, we expect the photoreactions to take the same course and to form similar products.

In order to compare our experimental results with calculations based on a statistical model of chain conformation, results are needed in an athermal solvent.<sup>18</sup> For polymethylene chains, an athermal solution is one in which the attractive and repulsive forces between  $\text{CH}_2$  pairs are exactly cancelled by those between  $\text{CH}_2$  groups and solvent molecules. Carbon tetrachloride has a very small heat of mixing with normal alkanes<sup>19</sup> and comes very close to satisfying these requirements.

**Proposed Mechanism.** The photochemical reaction of the general probe molecule **I** is depicted in Scheme I. Excitation of **I** produces the ketone singlet state which rapidly undergoes intersystem crossing to the lowest triplet state with unit efficiency. The benzophenone triplet state in  $\text{I}^*3$  phosphoresces with a rate constant  $k_p = 180 \text{ s}^{-1}$ .<sup>17</sup> It can also decay radiationlessly to the

ground state by a number of chain length independent processes. The first-order rate constant,  $k_d$ , which describes the sum of these processes, depends mainly on the purity of the solvent. Bimolecular self-quenching is represented by the rate constant  $k_{sq}$ . Intramolecular quenching,  $k_{iq}(n)$ , is the product of  $K(n)$ , the equilibrium constant for formation of the quenching complex, and  $k$ , the radiationless decay rate constant for the complex to decompose to products or the ground state.

The rate constants above may be calculated by using the modified Stern-Volmer equation

$$1/\tau_n = 1/\tau_n^0 + k_{sq}^{(2)}[I] \quad (1)$$

where  $k_{sq}^{(2)}$  is the rate constant for bimolecular self-quenching and  $\tau_n^0$  is the lifetime of **I** extrapolated to infinite dilution. It is insensitive to trace impurities in **I**. The reciprocal triplet lifetime at infinite dilution is equal to the sum of all unimolecular deactivation processes, i.e.

$$1/\tau_n^0 = k_p + k_d + k_{iq}(n) \quad (2)$$

However, since  $k_p + k_d$  are known to be independent of chain length,<sup>17</sup> the reciprocal lifetime of 4-carboxymethylbenzophenone **M-0** in the same batch of solvent should be equal to this sum. Thus

$$1/\tau_n^0 - 1/\tau_{\text{M-0}} = k_{iq}(n) \quad (3)$$

The rate constant  $k_{iq}(n)$  is a measure of the chain length dependent total intramolecular quenching. In the case where  $\text{Q} = \text{CH}_3$ ,  $k_{iq}(n)$  describes hydrogen abstraction from the unactivated methylene groups in the chain, since the methyl group reacts with a much slower rate.<sup>20</sup>

$$k_{iq}(n) = k_H(n) = \sum k_{H,i} \quad (4)$$

However if  $\text{Q} = \text{CH}=\text{CH}_2$ , two competing intramolecular processes can occur. The first is quenching due to the interaction between the excited-state ketone and the olefin,  $k_O(n)$ , and the second is quenching by hydrogen abstraction,  $k_H(n)$ , viz.

$$k_O(n) = k_{iq}(n) - k_H(n) \quad (5)$$

## Experimental Section

The synthesis and characterization of the molecules **O-n** will be reported elsewhere.<sup>21a</sup> Carbon tetrachloride and acetic acid were purified as described previously.<sup>17</sup> Samples (2.0 mL) were placed in cylindrical Pyrex cells (13 mm o.d.  $\times$  30 mm) fitted to a joint for attachment to a vacuum line. These were rigorously degassed by five successive freeze-pump-thaw cycles and sealed under a vacuum better than  $1 \times 10^{-5}$  torr.

For the phosphorescence decay measurements, six samples were placed in a temperature-controlled aluminum block, capable of rotating successive samples into the optical path. A nitrogen laser (NRG, Model 0.5-5-150/B) was used as the excitation source. Phosphorescence was detected at  $90^\circ$  to the excitation with a Hamamatsu 928 photomultiplier tube, connected via an operational amplifier to a Biomation 8100 waveform recorder. This in turn was interfaced to a Nuclear Data multichannel analyzer, where repeated scans could be summed. Typically 3 to 20 decays were summed for each sample at each temperature. In early experiments accumulated data in the multichannel analyzer were obtained in the form of punched paper tape and analyzed by a computer. More recently the Biomation 8100 has been interfaced directly to a Tektronix 4052 graphics microprocessor.

## Results

**Determination of Rate Constants and Activation Energies.** All phosphorescence decays were exponential. Samples of the benzophenone esters **O-n** showed a decrease in the triplet lifetime relative to the lifetime of 4-carboxymethylbenzophenone **M-0**, in the same solvent. This decrease was found to be proportional to the concentration of the ester in the sample. Typical data are presented for **O-11** in Table I. The variation in the lifetimes gave essentially linear fits to eq 1, yielding values of  $k_{sq}^{(2)}$  from the slope and  $\tau_n^0$  from the intercept. Values of  $k_{iq}(n)$  were obtained from

(20) (a) L. Giering, M. Berger, and C. Steel, *J. Am. Chem. Soc.*, **96**, 953 (1974). (b) P. J. Wagner, *Acc. Chem. Res.*, **4**, 168 (1971).

(21) (a) A. Mar, P. Svirskaya, and M. A. Winnik, *J. Org. Chem.*, submitted. (b) A. Mar, A. E. C. Redpath, and M. A. Winnik, *Nouv. J. Chem.*, **7**, 7 (1983).

(14) U. Maharaj and M. A. Winnik, *J. Am. Chem. Soc.*, **103**, 2328 (1981).

(15) T. Wilson and A. M. Halpern, *J. Am. Chem. Soc.*, **103**, 2412 (1981).

(16) (a) P. J. Wagner and E. J. Siebert, *J. Am. Chem. Soc.*, **103**, 7329 (1981). (b) R. R. Sauers and T. R. Henderson, *J. Org. Chem.*, **39**, 1850 (1974).

(17) M. A. Winnik and A. Lemire, *Chem. Phys. Lett.*, **46**, 283 (1977).

(18) J. H. Hildebrand, J. M. Prausnitz, and R. L. Scott, "Regular and Related Solutions", Van Nostrand Reinhold, New York, 1970.

(19) (a) J. R. Goates, R. J. Sullivan, and J. B. Ott, *J. Phys. Chem.*, **73**, 589 (1963). (b) V. Mathot and A. Deamyter, *J. Chem. Phys.*, **21**, 782 (1953).

**Table I.** Lifetime ( $\mu\text{s}$ ) of 12-Tridecyl 4-Benzoylbenzoate in  $\text{CCl}_4$ 

[ester], M	temperature, °C									
	24.2	-18.0	-5.1	2.8	19.6	39.1	61.2	81.0	101.8	23.6
<b>O-11</b> , $9.723 \times 10^{-4}$	5.06	10.3	8.65	7.19	5.58	4.24	3.44	2.58	2.12	5.17
<b>O-11</b> , $1.945 \times 10^{-3}$	4.63	9.58	7.86	6.96	5.20	3.97	3.16	2.38	1.94	4.8/
<b>O-11</b> , $3.889 \times 10^{-3}$	4.22	8.19	7.45	6.44	4.88	3.53	2.81	2.19	1.82	4.13
<b>O-11</b> , $5.834 \times 10^{-3}$	3.67	7.34	6.80	5.98	4.49	3.40	2.67	2.11	1.68	3.76
<b>O-11</b> , $9.723 \times 10^{-3}$	3.17	5.98	5.33	5.27	3.69	2.88	2.18	1.72	1.42	3.17
<b>M-0</b> , $5.411 \times 10^{-4}$	112.7	190.2	208.6	181.4	153.4	112.2	99.1	85.9	69.3	164.7

**Table II.** Intra- and Intermolecular Quenching Rate Constants for 12-Tridecyl 4-Benzoylbenzoate (**O-11**) in  $\text{CCl}_4$ 

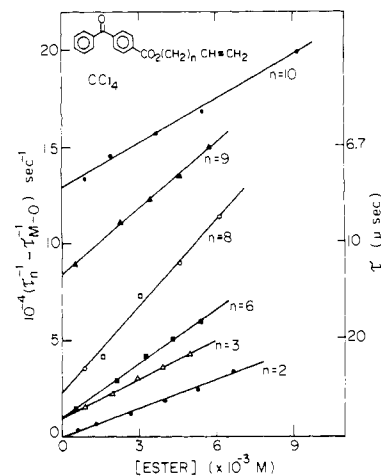
T, K	$k_{\text{O}_q(11)}$ ( $\times 10^4 \text{ s}^{-1}$ )	$k_q^{(2)}(11)$ ( $\times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ )	$r$
255.0	8.4	6.7	0.999
267.9	10.2	7.6	0.986
275.8	12.7	5.9	0.999
292.6	16.2	10.1	0.994
296.6	17.6	13.9	0.998
297.2	17.9	13.4	0.996
312.1	21.8	12.6	0.993
334.1	26.6	19.4	0.994
354.0	35.9	22.6	0.988
374.8	43.9	28.4	0.995

eq 3. Once the rate constants  $k_{\text{iq}}(n)$  and  $k_{\text{sq}}^{(2)}$  were obtained at various temperatures (cf. Table II), the activation energies, enthalpies, and entropies could be calculated respectively from plots of  $\ln k$  vs.  $1/T$  or  $\ln(k/T)$  vs.  $1/T$ . Density changes with temperature<sup>22</sup> were taken into account. In carbon tetrachloride solution, there is a 2% increase in volume at 100 °C relative to that at 25 °C, whereas for acetic acid the change is 9%. Density corrections were extrapolated to -10 °C in supercooled acetic acid. Two identical sets of samples were prepared and degassed. For one set of samples, the rate constants were obtained in the following order: room temperature, lowest temperature to the highest temperature in eight increments, and finally room temperature again. For the second set of samples, the rate constants were determined first at room temperature, then at the highest temperature to the lowest temperature in eight increments and, again, at room temperature. The formation of photoproducts was not found to affect significantly our results in any of the olefin esters studied, and the Arrhenius plots obtained from these two sets of experiments were virtually superimposable. This was not the case for acetylene esters<sup>21</sup> ( $Q = \text{C}\equiv\text{CH}$  in Scheme I).

Values of the intramolecular quenching rate constants  $k_{\text{iq}}(n)$  and the bimolecular self-quenching rate constants  $k_{\text{sq}}^{(2)}$  at 25 °C are presented in Table III for experiments in  $\text{CCl}_4$  and in Table IV for experiments in acetic acid. Also presented are the activation parameters for each reaction. Errors in the rate constants are  $\pm 5\%$ . Error limits reported for  $E_a$ ,  $\Delta H$ , and  $\Delta S$  are one standard deviation.

**Bimolecular Interactions.** The triplet state of benzophenone-4- $\text{CO}_2\text{CH}_3$  is quenched by simple monosubstituted alkenes in carbon tetrachloride solution with a rate constant  $k_q^{(2)}$  of ca.  $7 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ . Maharaj reported a value of  $7.1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  for 1-hexene<sup>14</sup> and we find  $6.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  for 1-pentene. Self-quenching rate constants  $k_{\text{sq}}^{(2)}$  for **O-n** have somewhat larger values. Although one might consider that interaction between the benzophenone units might lead to phosphorescence quenching,  $\tau$  values for **M-0**, for various concentrations up to  $5 \times 10^{-3} \text{ M}$ , were essentially identical. Consequently self-quenching in the **O-n** samples is due to interaction of the excited ketone with the side chain of a second molecule.

There is also a solvent effect on chromophore reactivity. For **M-0**<sup>3</sup> + 1-pentene, we find that  $k_q^{(2)}$  is 2.6 times larger in acetic acid than in carbon tetrachloride. Similarly for self-quenching in **O-n**, we note that  $k_{\text{sq}}^{(2)}$  values are ca. 2.7 times larger in HOAc

**Figure 1.** Stern-Volmer plots of  $\alpha,\omega$ -alkenyl 4-benzoylbenzoate esters, **O-n**, in  $\text{CCl}_4$  at 22 °C.

than in  $\text{CCl}_4$ . The origin of this effect is not understood. A similar effect has been reported for hydrogen abstraction reactions of **M-0**<sup>3</sup> with normal alkanes.<sup>23</sup> Here  $k_q^{(2)}(\text{HOAc})/k_q^{(2)}(\text{CCl}_4) = 1.35$ .

One of the delicate aspects of kinetic studies involving phosphorescence quenching is that traces of quenching impurities, undetected in conventional analyses, can have a serious effect on the determination of rate constants. Self-quenching bimolecular rate constants are sensitive to impurities in the ketone sample: the impurity concentration increases in proportion to the ketone concentration. For a  $k_{\text{sq}}^{(2)}$  value of ca.  $5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ , an impurity of a diffusion-controlled quencher at the 0.01% level would have a serious effect on the slope of the Stern-Volmer plot, eq 6. It would not, however, affect the intercept value.

The way in which these factors operate can be seen in Figure 1, where we have plotted  $(1/\tau_n - 1/\tau_{\text{M-0}})$  vs. [ester] concentration for a series of **O-n** samples in  $\text{CCl}_4$  at room temperature. The most important feature of these data is that the slopes are quite similar. A corresponding plot for the methyl ester **M-0** has zero slope in this concentration range (i.e.,  $(k_{\text{sq}}^{(2)} < 1 \times 10^4 \text{ M}^{-1} \text{ s}^{-1})$ ).

It is tempting to attribute the small differences in slope seen in Figure 1, as well as the differences in  $k_{\text{sq}}^{(2)}$  values reported in Table II, to the presence of trace amounts of impurities in some of the samples. It is more difficult to ascribe to impurities the observation that all of the  $k_{\text{sq}}^{(2)}$  values are significantly larger than those found for the quenching of **M-0**<sup>3</sup> by 1-pentene and 1-

(23) (a) M. A. Winnik, S. N. Basu, C. K. Lee, and D. S. Saunders, *J. Am. Chem. Soc.*, **98**, 2928 (1976). (b) M. A. Winnik, A. Lemire, D. S. Saunders, and C. K. Lee, *J. Am. Chem. Soc.*, **98**, 2000 (1976). (c) M. A. Winnik, C. K. Lee, S. Basu, and D. S. Saunders, *J. Am. Chem. Soc.*, **96**, 6182 (1974).

(24) D. Bichan and M. A. Winnik, *Tetrahedron Lett.*, 3857 (1974).

(25) C. Galli, G. Illuminati, L. Mandolini, and P. Tamborra, *J. Am. Chem. Soc.*, **99**, 2591 (1977).

(26) H. Kwart, D. A. Benko, and M. E. Bromberg, *J. Am. Chem. Soc.*, **100**, 7093 (1978).

(27) (a) H. Morawetz, *Pure Appl. Chem.*, **38**, 267 (1974). (b) M. I. Page, *Chem. Soc. Rev.*, **2**, 295 (1973).

(28) S. J. Fraser and M. A. Winnik, *J. Chem. Phys.*, **75**, 4683 (1981).

(29) (a) D. S. Saunders and M. A. Winnik, *Macromolecules*, **11**, 18, 25 (1978). (b) M. A. Winnik, R. E. Trueman, G. Jackowski, D. S. Saunders, and S. G. Whittington, *J. Am. Chem. Soc.*, **96**, 4843 (1974). (c) S. J. Fraser and M. A. Winnik, *J. Chem. Phys.*, **72**, 728 (1980). (d) S. J. Fraser and M. A. Winnik, *J. Chem. Phys.*, **70**, 575 (1979).

(22) (a) J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds", Vol. 2, Elsevier, New York, 1965, pp 184 and 434. (b) J. M. Costello and S. T. Bowden, *Recl. Trav. Chim. Pays-Bas*, **77**, 803 (1958).

Table III. Rate and Thermodynamic Constants for  $\omega$ -Alkenyl 4-Benzoylbenzoates in  $\text{CCl}_4$ 

ester	quenching rate (25 °C)	$A$	$E_a$ , kcal/mol	$r$	$\Delta H^\ddagger$ , kcal/mol	$\Delta S^\ddagger$ , eu
	$k_{Oq}(n) (\times 10^4 \text{ s}^{-1})$	$A \times 10^6 \text{ s}^{-1}$				
O-6	0.4					
O-8	2.7	6.1	$3.19 \pm 0.11$	0.995	$2.58 \pm 0.11$	$-29.5 \pm 0.4$
O-9	9.5	6.0	$2.44 \pm 0.10$	0.997	$1.85 \pm 0.1$	$-29.6 \pm 0.4$
O-10	12.6	10.1	$2.59 \pm 0.09$	0.998	$1.99 \pm 0.09$	$-28.5 \pm 0.3$
O-11	16.9	11.1	$2.45 \pm 0.07$	0.997	$1.83 \pm 0.07$	$-28.5 \pm 0.3$
O-12	28.2	24.7	$2.62 \pm 0.15$	0.991	$2.03 \pm 0.15$	$-26.7 \pm 0.5$
O-13	26.8	15.6	$2.42 \pm 0.09$	0.997	$1.81 \pm 0.09$	$-27.7 \pm 0.3$
O-14	22.1	10.8	$2.32 \pm 0.11$	0.995	$1.74 \pm 0.11$	$-28.3 \pm 0.4$
O-15	19.8	24.5	$2.87 \pm 0.10$	0.996	$2.25 \pm 0.11$	$-26.8 \pm 0.4$
O-18	20.6	18.7	$2.71 \pm 0.13$	0.994	$2.08 \pm 0.13$	$-27.4 \pm 0.4$
O-21	15.5	19.6	$2.78 \pm 0.3$	0.990	$2.19 \pm 0.3$	$-27.2 \pm 0.8$
	$k_q^{(2)}(n) (\times 10^7 \text{ M}^{-1} \text{ s}^{-1})$	$A \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$				
O-6	1.10	3.68	$2.05 \pm 0.07$	0.998	$1.44 \pm 0.08$	$-21.4 \pm 0.3$
O-8	1.41	4.52	$2.05 \pm 0.08$	0.997	$1.45 \pm 0.09$	$-21.0 \pm 0.3$
O-9	0.96	2.48	$1.97 \pm 0.13$	0.992	$1.38 \pm 0.12$	$-22.1 \pm 0.4$
O-10	0.77	3.03	$2.21 \pm 0.22$	0.983	$1.62 \pm 0.22$	$-21.7 \pm 0.8$
O-11	1.08	3.23	$2.03 \pm 0.11$	0.994	$1.44 \pm 0.11$	$-21.5 \pm 0.4$
O-18	1.21	9.35	$2.59 \pm 0.15$	0.989	$1.96 \pm 0.16$	$-19.6 \pm 0.5$
1-pentene	0.62					

Table IV. Rate and Thermodynamic Constants for  $\omega$ -Alkenyl 4-Benzoylbenzoates in HOAc

ester	quenching rate, (25 °C)	$A$	$E_a$ , kcal/mol	$r$	$\Delta H^\ddagger$ , kcal/mol	$\Delta S^\ddagger$ , eu
	$k_{Oq}(n) (\times 10^5 \text{ s}^{-1})$	$A \times 10^7 \text{ s}^{-1}$				
O-6	0.13					
O-8	2.47	4.14	$3.00 \pm 0.16$	0.990	$2.38 \pm 0.16$	$-25.8 \pm 0.6$
O-9	5.43	6.79	$2.79 \pm 0.23$	0.979	$2.18 \pm 0.23$	$-24.8 \pm 0.8$
O-10	5.52	6.23	$2.80 \pm 0.27$	0.975	$2.19 \pm 0.27$	$-24.9 \pm 0.8$
O-11	5.70	6.85	$2.85 \pm 0.18$	0.987	$2.25 \pm 0.19$	$-24.7 \pm 0.6$
O-12	8.15	12.6	$2.99 \pm 0.13$	0.995	$2.40 \pm 0.14$	$-23.5 \pm 0.5$
O-13	6.73	7.53	$2.79 \pm 0.13$	0.994	$2.17 \pm 0.14$	$-24.5 \pm 0.4$
O-14	6.65	7.47	$2.77 \pm 0.13$	0.993	$2.15 \pm 0.13$	$-24.6 \pm 0.5$
O-15	5.88	7.06	$2.83 \pm 0.16$	0.992	$2.22 \pm 0.16$	$-24.7 \pm 0.5$
O-18	4.38	7.50	$3.00 \pm 0.22$	0.992	$2.35 \pm 0.22$	$-24.7 \pm 0.6$
O-21	4.01	5.51	$2.91 \pm 0.27$	0.987	$2.23 \pm 0.27$	$-25.4 \pm 0.8$
	$k_q^{(2)}(n) (\times 10^7 \text{ M}^{-1} \text{ s}^{-1})$	$A \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$				
O-6	2.54	0.95	$2.16 \pm 0.08$	0.993	$1.55 \pm 0.08$	$-19.5 \pm 0.3$
O-8	2.98	0.99	$2.08 \pm 0.21$	0.985	$1.48 \pm 0.22$	$-19.4 \pm 0.7$
O-9	2.77	1.58	$2.59 \pm 0.22$	0.980	$1.97 \pm 0.23$	$-18.5 \pm 0.7$
O-11	2.78	0.85	$2.01 \pm 0.12$	0.990	$1.38 \pm 0.13$	$-19.8 \pm 0.4$
O-15	3.76	2.89	$2.53 \pm 0.14$	0.994	$1.91 \pm 0.14$	$-17.3 \pm 0.5$
1-pentene	1.60					

hexene. For example, we determined  $k_q^{(2)}$  in  $\text{CCl}_4$  to be  $6.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  for 1-pentene. For self-quenching of **O-n** in  $\text{CCl}_4$ , an average value of  $1.1 \times 10^7$  is calculated. In acetic acid, we determined  $k_q^{(2)}$  for **M-0**\*<sup>3</sup> + 1-pentene to be  $1.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ , whereas the average self-quenching values for **O-n**, is  $3.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ . Another rationale is that a ketone exciplex of the sort suggested by Singer<sup>30</sup> is involved in the self-quenching reaction. It may be ineffective at quenching **M-0**\*<sup>3</sup>, but it might hold the two aromatic chromophores together sufficiently to enhance the efficiency of reaction with the side chain.

At elevated temperatures, both the slopes and intercepts of the Stern-Volmer plots increase (Figure 2). These changes provide information on the activation energies respectively of bimolecular and intramolecular quenching processes. The activation energies for bimolecular quenching are chain length independent. They were found to be 2.16 kcal/mol in  $\text{CCl}_4$  and 2.27 kcal/mol in HOAc (Tables III and IV). In carbon tetrachloride the activation energy is 0.4 kcal/mol higher than that observed<sup>14</sup> for the quenching of **M-0**\*<sup>3</sup> by 1-hexene.

**Intramolecular Quenching.** In the previous section we noted that trace impurities in the ketone samples could affect the apparent  $k_{sq}^{(2)}$  values. These have no effect on the intercepts of the Stern-Volmer plots, eq 6, from which  $k_{iq}$  values are calculated. On the other hand, solvent impurities and solvent reactivity affect the value of the intercept. The data analysis must take these

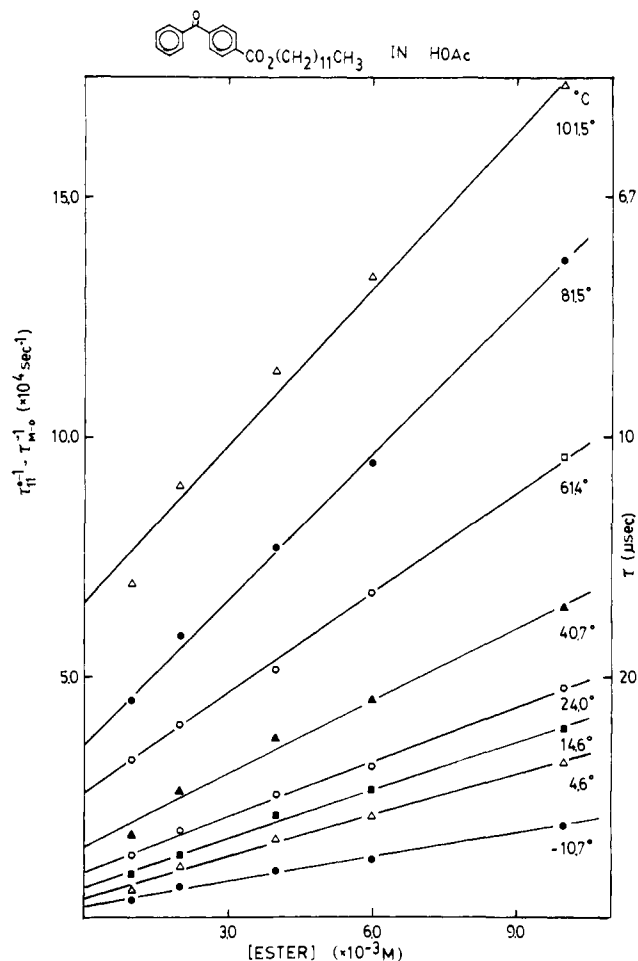
factors into account. What one assumes is that these factors contribute equally to the quenching of **O-n**\*<sup>3</sup> and **M-0**\*<sup>3</sup>. If one measures  $\tau_n^\circ$  and  $\tau_{M-0}$  in the same batch of solvent, one can obtain  $k_{iq}(n)$  values via eq 3. This has the effect of relegating the solvent reactivity and solvent impurity contributions to the triplet lifetime to the  $k_d$  term in eq 2. We emphasize that the measurement of  $\tau_{M-0}$  has to be made with great care, since all the different  $k_{iq}^{(n)}$  values depend upon it.

Our concern with end-to-end cyclization in **O-n** made it necessary to separate the various contributors to the intramolecular quenching process described by  $k_{iq}(n)$ . These are quenching by the olefin  $k_O(n)$  and quenching by hydrogen abstraction  $k_H(n)$ . In order to determine  $k_O(n)$ , the intramolecular hydrogen abstraction rate constants  $k_H(n)$  were determined for a homologous series of *n*-alkyl esters of benzophenone-4-carboxylic acid. These values were used as a reasonable estimate for hydrogen abstraction rates in the molecules **O-n**. In this manner,  $k_O(n)$  was obtained from the relationship

$$k_O(n) = k_{iq}(n) - k_H(n) \quad (6)$$

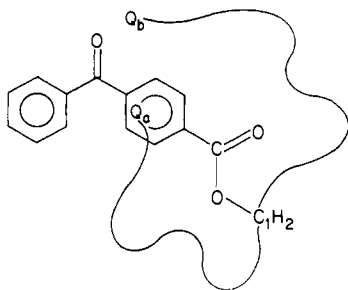
The relative magnitudes of these three terms can be seen in Figures 3 and 4. Hydrogen abstraction is negligible for  $n < 10$ . The rate constant  $k_H(n)$  increases linearly with  $n$ , and for  $n = 21$ , the longest chain we examined, it contributes ca. 35% of the total intramolecular quenching in  $\text{CCl}_4$  and ca. 20% in acetic acid. The values of  $k_O(n)$  show a similar dependence on chain length in both  $\text{CCl}_4$  (Figure 3) and HOAc (Figure 4). For short chains,  $n < 8$ , no quenching occurs. The value of  $k_O(n)$  increases markedly

(30) M. W. Wolf, R. E. Brown, and L. A. Singer, *J. Am. Chem. Soc.*, **91**, 2478 (1969).



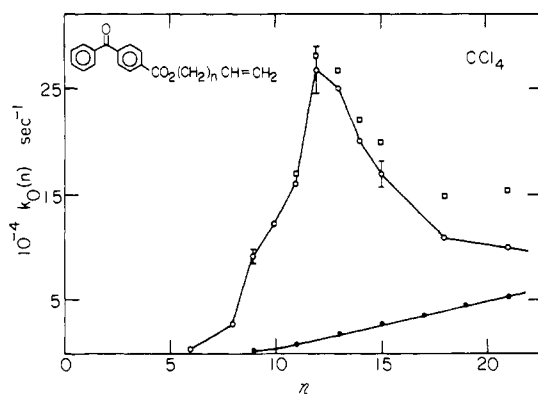
**Figure 2.** Stern-Volmer plots ( $\tau^{-1} - \tau_{M,0}^{-1}$ ) vs. the concentration of **O-8** in acetic acid at various temperatures.

for longer chains and maximizes for a chain containing 12 methylene groups. A gradual decrease in the rate of intramolecular quenching occurs when  $n > 12$ . The kinetic behavior of short-chain derivatives of **O-*n*** may be understood in terms of the geometric requirements of the intramolecular quenching process. The ester group is known to be planar due to conjugation with the aryl ring. The *trans* conformation is preferred (*vide infra*). Space-filling molecular models indicate that the alkene may reside

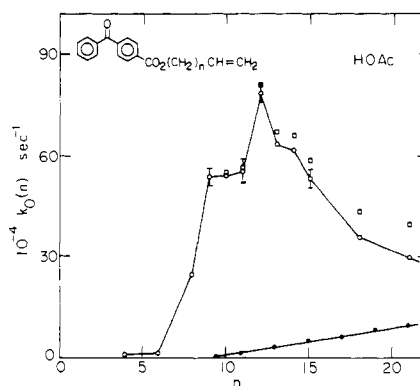


over the nearer benzene ring ( $Q_a$ ) for  $n = 4$  but may not come in contact with the ketone carbonyl ( $Q_b$ ) until there are eight methylene groups in the chain. Intramolecular quenching is only observed for chains of eight or more  $CH_2$  groups. The oxetane formed by the intramolecular photoreaction of **O-9** has been isolated by Bichan and Winnik.<sup>24</sup> Intramolecular quenching and chemical product formation must have similar geometric requirements, which require the alkene to be in close proximity to the ketone carbonyl.

Once  $n > 12$ , the steric constraints are relaxed, and the chain has access to many "strain-free" conformations which permit it to achieve proximity to the reactive site. For these chains, the



**Figure 3.** Intramolecular quenching rate constants as a function of chain length in  $CCl_4$  at 25 °C: ( $\square$ ) values of  $k_{iq}(n)$  for the total quenching in **O-*n***; ( $\circ$ ) values of  $k_H(n)$  for quenching by hydrogen abstraction in benzophenone-4- $CO_2(CH_2)_nCH_3$ ; ( $\circ$ ) values of  $k_O(n)$  for intramolecular quenching in **O-*n*** by the  $CH=CH_2$  group. Error bars represent one standard deviation.



**Figure 4.** Intramolecular quenching rate constants as a function of chain length in acetic acid at 25 °C (cf. Figure 3): ( $\square$ )  $k_{iq}(n)$ ; ( $\circ$ )  $k_H(n)$ ; ( $\circ$ )  $k_O(n)$ .

major factor which affects the chain length dependence of  $k_O(n)$  is that of the probability of finding the quencher in the reactive volume about the carbonyl oxygen. This cyclization property is sensitive only to the conformational properties of the chain. It varies with chain length. Our experiments which determine  $k_O(n)$  provide a measure of this cyclization probability.

It should be emphasized that  $k_O(n)$  is proportional to the cyclization *probability* and not the cyclization *dynamics* of the chain. The quenching reaction we examine is inefficient. Only one encounter per 100 is effective at quenching the triplet state of **O-*n***. Therefore, the intramolecular quenching step is preceded by a conformational equilibrium. The observed rate constant is a product of these two terms,  $k_{iq}(n) = K(n)k$ .

**Variation of  $k_{iq}$  with Temperature.** A study of the temperature dependence of  $k_{sq}^{(2)}$  and  $k_{iq}(n)$  allows one to obtain the activation energy for both the intra- and intermolecular quenching processes. In acetic acid, for  $n \geq 8$ , the activation energies for intramolecular quenching are chain length independent. An average  $E_a(HOAc) = 2.87$  kcal/mol was obtained. In carbon tetrachloride, the  $E_a$  values are virtually identical for  $n > 8$ , with a mean value of 2.6 kcal/mol. For  $n = 8$ ,  $E_a$  is significantly larger, with a value of 3.2 kcal/mol. We take this as an indication that the reactive geometry in **O-8** is somewhat distorted relative to that in molecules with  $n > 8$ , or that cyclization is accompanied by ring strain.

When one talks about activation energies in terms of ring strain contributions to a reaction, one must keep in mind that several factors can contribute to the temperature sensitivity of the reaction rate. Likely candidates are torsional strain, changes in the gauche/trans (*g/t*) conformational population, or the presence of high-energy conformational sequences. For example, adjacent gauche bonds of the opposite sense  $g^+g^-$  are 2 kcal/mol higher in energy than  $g^+g^+$  or  $g^-g^-$  pairs—a factor referred to as the

**Table V.** Arrhenius Parameters for Total Intramolecular Quenching and for Quenching by the Terminal Alkene

solvent	ester	$A_{\text{obsd}}^a$ ( $\times 10^7 \text{ s}^{-1}$ )	$E_a(\text{obsd})^a$ kcal/mol	$A_0^b$ ( $\times 10^7 \text{ s}^{-1}$ )	$E_a(\text{O})^b$ kcal/mol
CCl <sub>4</sub>	<b>O-11</b>	1.11	2.45 ± 0.07	0.87	2.31 ± 0.0
	<b>O-13</b>	1.56	2.42 ± 0.09	1.16	2.27 ± 0.1
	<b>O-15</b>	2.45	2.87 ± 0.10	1.32	2.58 ± 0.1
HOAc	<b>O-11</b>	6.85	2.85 ± 0.18	6.15	2.80 ± 0.1
	<b>O-13</b>	7.53	2.79 ± 0.13	6.77	2.76 ± 0.1
	<b>O-15</b>	7.06	2.83 ± 0.16	3.66	2.53 ± 0.1

<sup>a</sup> From plots of  $\ln k_{\text{iq}}(n)$  vs.  $1/T$ . <sup>b</sup> From plots of  $\ln k_{\text{O}}(n)$  vs.  $1/T$ , i.e., corrected for hydrogen abstraction.

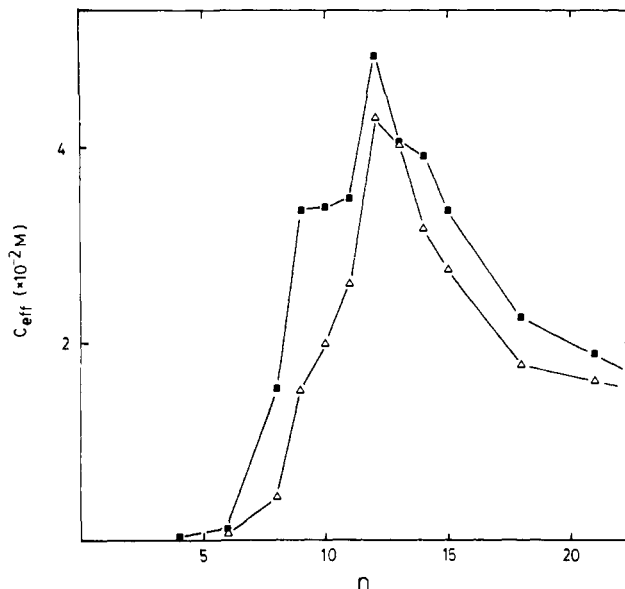
pentane effect.<sup>1</sup> If cyclization were strain free, one might expect the  $E_a$  values for intramolecular quenching to be identical with that for the corresponding bimolecular reaction. Illuminati<sup>25</sup> showed that  $E_a$  values for lactone formation to form a 23-membered ring were identical to those for bimolecular ester formation.

In all of our examples  $E_a(\text{intra})$  is ca. 1 kcal/mol higher than the  $E_a(\text{inter})$  value reported by Winnik and Maharaj for the quenching of **M-0**\*<sup>3</sup> by 1-hexene.<sup>14</sup> Molecular models indicate no need for torsional distortions for cyclization. A computer model (see below) suggests that the fraction of gauche bonds is similar in the ensemble of a conformation of **O-n** and in the small subset of cyclized conformations. We note that  $g^{\pm}g^{\mp}$  sequences are very effective in forcing a chain to fold back upon itself. While these pairs are very improbable at ordinary temperatures they become more accessible as the temperature increases. Hence we can rationalize our observations of larger  $E_a$  values for the intramolecular reaction in terms of a small number of chains with  $g^{\pm}g^{\mp}$  sequences which are particularly effective at enhancing cyclization.

Since both hydrogen abstraction and quenching by the alkene group contribute to  $k_{\text{iq}}(n)$ , we were concerned about the influence of the former on the  $E_a$  values calculated from  $k_{\text{iq}}(n)$  data. Bimolecular hydrogen abstraction by **M-0**\*<sup>3</sup> is characterized by a much larger activation energy (3.8 kcal/mol) than is quenching by 1-alkenes (1.8 kcal/mol). In order to assess the magnitude of the problem, we determined  $k_{\text{H}}(n)$  values as a function of temperature for **Q-n** ( $n = 11, 13, 15$ ;  $Q = \text{CH}_3$ ). We calculated  $k_{\text{O}}(n)$  values at each temperature according to eq 8, and subsequently we used these values to obtain "true"  $E_a(\text{O})$  values. As indicated in Table V, the  $E_a(\text{O})$  values are only 0.1 to 0.3 kcal/mol smaller than the  $E_a(\text{obsd})$  values obtained from Arrhenius plots of total intramolecular quenching ( $k_{\text{iq}}(n)$ ). No attempt has been made to correct the data for allylic hydrogen abstraction. This correction, however, is expected to be small, since Wagner<sup>20b</sup> has shown that the rate constant for intramolecular allylic hydrogen abstraction is only four times larger than that from an unactivated methylene group. In addition, our experiments (Figures 3 and 4) indicate that quenching by the olefin is much faster than the total quenching by hydrogen abstraction in the chain.

Throughout the course of this discussion, quenching by the olefin was assumed to arise via an exciplex intermediate, whereas quenching by hydrogen abstraction was not attributed to an exciplex being formed. Exciplex formation involves the interaction between the  $n$  orbital of the ketone carbonyl oxygen and the  $\pi$  orbital of the alkene.<sup>13,16</sup> Recent experiments by Kwart, involving allylic hydrogen abstraction by *tert*-butoxy radicals, have led him to propose the formation of a charge-transfer complex between the  $p$  orbital of the *tert*-butoxy radical and the  $\pi$  system of the olefin as a reaction intermediate.<sup>26</sup> This allows the orthogonal  $p$  orbital to form a five-membered cyclic transition state from which H transfer takes place. If allylic hydrogen abstraction in **O-n** occurs via a ketone-alkene complex, its contribution to the reaction rate should be included in any consideration of the cyclization properties of the chain.

**Solvent Effects.** Protic solvents affect the triplet reactivity of the benzophenone chromophore. The solvent effect on the quenching reaction may be obtained from the kinetic study of the bimolecular reaction between **M-0**\*<sup>3</sup> and 1-pentene. The ratio of the bimolecular quenching rate constants for this reaction is  $k_{\text{q}}^{(2)}(\text{HOAc})/k_{\text{q}}^{(2)}(\text{CCl}_4) = 2.58$ . This value shows that polar



**Figure 5.** The effective concentration ( $C_{\text{eff}}$ ) as a function of chain length for benzophenone-4- $\text{CO}_2(\text{CH}_2)_n\text{CH}=\text{CH}_2$  in  $\text{CCl}_4$  ( $\Delta$ ) and acetic acid ( $\blacksquare$ ).

solvents enhance the photoreactivity of the **M-0** chromophore.

Solvent effects on the intrachain reaction rate can arise from two sources. Higher values of  $k_{\text{O}}(n)$  observed in HOAc relative to  $\text{CCl}_4$  may be due to the enhanced reactivity of the excited chromophore in HOAc. In addition the solvent might affect chain conformation to perturb the cyclization probability. One method of separating these two contributions is to normalize the  $k_{\text{O}}(n)$  by dividing them by the  $k_{\text{q}}^{(2)}$  value for the model reaction between **M-0**\*<sup>3</sup> and 1-pentene. If one assumes that the characteristic reactivity of the two functional groups is the same in both the intra- and intermolecular reactions, this treatment removes the contribution of chromophore reactivity from  $k_{\text{O}}(n)$ . The ratio  $k_{\text{O}}(n)/k_{\text{q}}^{(2)}$  has units of moles/litre and is often called the effective concentration  $C_{\text{eff}}$ .<sup>27</sup>  $C_{\text{eff}}$  values for reactions in HOAc and  $\text{CCl}_4$  can be compared to determine the solvent effect on chain shape.

These  $C_{\text{eff}}$  values are plotted vs. chain length in Figure 5. Much of the difference between the values of  $k_{\text{O}}(n)$  in HOAc and  $\text{CCl}_4$  has been removed. Small differences remain, however, especially for short chains where  $n = 8-11$ . The results imply that in acetic acid there are factors which cause small enhancements in the end-to-end cyclization probability of the chains.

The solvent is unlikely to cause any gross perturbations in the available conformations of chains with 8-11 carbons. Our results are consistent with very small changes in the reaction geometry accounting for the faster reactivity at  $n = 8$  in HOAc. If we were forced to try to explain the small increase in  $C_{\text{eff}}$  in HOAc for 9-, 10-, and 11-carbon chains, we might invoke a small enthalpic preference for the chain end to be near the chromophore rather than surrounded by polar solvent.

**Conformation and Cyclization Probability.** The rate constants  $k_{\text{O}}(n)$  provide values which can be interpreted in terms of the cyclization properties of the chain connecting the aromatic ketone and  $\text{CH}=\text{CH}_2$  groups. We have argued in preceding sections that this quenching is an inefficient process; hence  $k_{\text{O}}(n)$  should be proportional to  $P_n$ , the cyclization probability of the chain. It is also useful to examine whether the chains are able to achieve conformational equilibrium on the time scale of the experiment. This time scale is determined by the benzophenone triplet state lifetime and is on the order of microseconds.

Some estimate of chain mobility can be obtained from <sup>13</sup>C NMR spin-lattice ( $T_1$ ) relaxation times. These were carried out in  $\text{CCl}_4$  in collaboration with Dr. Ph. Dais.<sup>31</sup> Correlation times

(31) (a) W. F. Reynolds, Ph. Dias, A. Mar, and M. A. Winnik, *J. Chem. Soc., Chem. Commun.*, 757 (1976). (b) Ph. Dias, Ph.D. Thesis, University of Toronto, 1980.

shown below were calculated from each of the  $T_1$  values for carbons of the chain whose resonances could be resolved. The calculations made the usual assumptions about extreme narrowing limit and isotropic motion.<sup>31</sup> While the correlation time is defined as the time for the  $^{13}\text{C}-\text{H}$  bond to rotate through an angle of one radian, we take this value as a semiquantitative insight into the motion of the various carbons of the chain. Typical correlation times are in the picosecond domain. Values of  $\tau_c$  for two molecules of interest are presented below, where **B** represents the para-substituted benzophenone moiety.

54.7 36.2 22.2 23.5 9.16 7.03 3.52 ps

**B**-CO<sub>2</sub>CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>12</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>

52.3 38.0 31.0 28.7 27.4 25.9 18.7 9.0 ps

**B**-CO<sub>2</sub>CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>14</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH=CH<sub>2</sub>

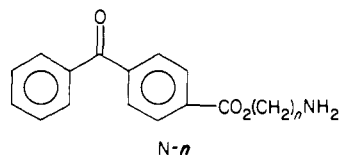
The motion of the chain members is dependent on both their position relative to the bulky benzophenone end group and on chain length. However,  $\tau_c$  values are indicative of a flexible chain. They suggest that hydrocarbon chains undergo large-amplitude changes on the time scale of 100–200 ps.

Rate constants themselves cannot be compared directly with calculations of cyclization probability based upon a theoretical model. The rate constants must first be transformed into quantities with the appropriate units. We choose the reaction of **M-0**<sup>3</sup> with 1-pentene as a model reaction and examine the ratio of  $k_0(n)$  to the second-order rate constant  $k_q^{(2)}$  for this process. These  $C_{\text{eff}}$  values are directly proportional to cyclization probability. Concentration is a measure of the probability of finding a species in a certain volume. If that volume  $V$  is the reactive space about the ketone carbonyl oxygen in **O-n** and  $N_A$  is Avagadro's number, we can write

$$C_{\text{eff}} = 1000P_n/N_A V \quad (7)$$

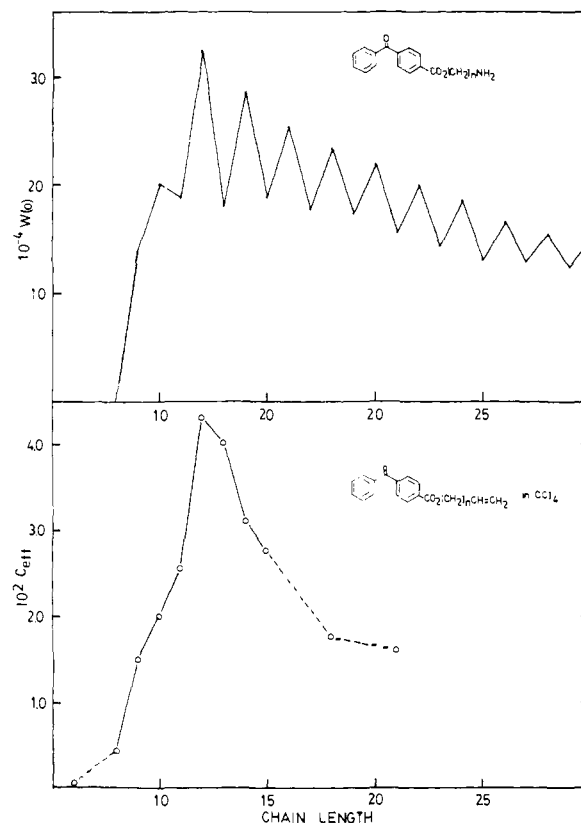
$C_{\text{eff}}$  thus measures the probability of the CH=CH<sub>2</sub> group being within the reactive volume.

**Theoretical Simulation of Cyclization.** In order to obtain theoretical values of  $P_n$ , a simulation of the cyclization process in **O-n** was undertaken in collaboration with Dr. S. Fraser.<sup>28</sup> This simulation used a lattice-based rotational isomeric state model for the polymethylene chain and took full account of the steric effects associated with the aromatic ketone group. Because it was not convenient to accommodate a CH=CH<sub>2</sub> group as a quencher in the simulation, an NH<sub>2</sub> group was used as the quenching moiety at the chain end. Details of the simulation have been published.<sup>28,29</sup> Only general features of the calculation are recounted here.



In the simulation, a large number of independent configurations of **N-n** were generated and tested to see if a reactive (cyclized) configuration was achieved. Cyclization was detected by defining a reactive volume centered about the ketone oxygen. A reactive configuration was defined by the presence of the amine nitrogen within the sphere ( $r = 3.1 \text{ \AA}$ ), with its nonbonded electrons pointing toward the oxygen atom. Monte Carlo methods were used to estimate partition functions for cyclized and total chains.  $P_n$  was obtained from their ratio. In carrying out the calculations, gauche bonds were disfavored by  $E_g = 600 \text{ cal/mol}$ . Adjacent  $g^+g^+$  sequences, normally unimportant at 25 °C for polymethylene chains, were suppressed entirely.

The computed values of  $P_n$  are shown in Figure 6. Cyclization has an onset: the end group must be able to reach the reactive volume before reaction can occur. The steep rise in  $P_n$  and  $C_{\text{eff}}$  is dependent both on the details of the chemical reaction and on the fact that the number of cyclized chain conformations increases faster with chain length than the total number of chains. For longer chains, the decrease in  $C_{\text{eff}}$  reflects the decrease in the



**Figure 6.** The end-to-end cyclization probability  $P_n$  for the molecules benzophenone-4-CO<sub>2</sub>(CH<sub>2</sub>)<sub>n</sub>NH<sub>2</sub> as a function of chain length. The data are taken from ref 28. The benzophenone-4-CO<sub>2</sub> group has two discrete conformations: one with the ester group syn to the ketone oxygen and one with it anti. These are essentially isoenergetic. The calculation assumes an equal number of molecules in each. The upper curve represents the sum of contributions to cyclization from molecules in the syn and anti conformations.<sup>28</sup>

cyclization probability. The alternating pattern in  $P_n$  is an artifact of the lattice-based model. Torsional oscillations about C-C bonds in real chains might be expected to smooth out this effect.

The entropy of cyclization may be calculated from  $\Delta S_{\text{cy}} = -R(\ln P_n)$ . These calculated values were found to be 10 cal deg<sup>-1</sup> mol<sup>-1</sup> less negative in value than those determined experimentally. If the predicted values are accurate, this difference can be associated with the entropy change in the chemical quenching step.

The computed cyclization probabilities allow one in principle to estimate the size of the reactive volume from eq 8. While the true size and shape of the reactive volume is not known, a  $C_{\text{eff}}$  value of  $3 \times 10^{-2} \text{ M}$  corresponds to a  $P_n$  value of  $3 \times 10^{-4}$  in a reactive volume of  $17 \text{ \AA}^3$ . This value for the size of the reactive volume is not totally unreasonable, although perhaps a bit small. It is satisfying that the RIS model can give one some quantitative insight into subtle features associated with an intramolecular chemical reaction.

The calculations indicate negligible changes in  $P_n$  over the temperature range of our experiments. This is a consequence of a very similar fraction of gauche bonds in the cyclized chains and in the total ensemble of chains for **N-n**. The activation energy difference we find for intramolecular and bimolecular quenching [ $E_a(\text{inter}) - E_a(\text{intra}) \approx 1 \text{ kcal/mol}$ ] in **O-n** must have a different origin. Molecular models indicate that  $g^+g^+$  sequences facilitate cyclization. While these conformational sequences are strongly disfavored at low temperatures, they have a large temperature coefficient. Thus if they make a non-negligible contribution to  $k_{\text{iq}}$  at lower temperatures, this contribution would increase with temperature and affect the experimental activation energy.

**Acknowledgment.** The authors thank NSERC Canada for their functional support. We are grateful to Dr. Photis Dais and Professor W. F. Reynolds for the  $^{13}\text{C}$  NMR  $T_1$  measurements.