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(17) If variations in chain length are neglected, then $\overline{\Delta C^\circ_p}$ for propagation is given by the difference in heat capacity of the monomer and the repeat unit of the polyene chain. For polymerization of acetylene, group additivity considerations similar to those outlined in the Appendix yield $\overline{\Delta C^\circ_p} = +0.08$ cal/K mol over the range 298 to 800 K.
(18) This is analogous to use of the modified Arrhenius equation, $k = A'T^n e^{-E/RT}$. The variables A' and E' are related to the usual Arrhenius parameters A and E by $A = A'(eT)^n$ and $E = E' + nRT$, where n is a small positive or negative integer.
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Photoreaction of Benzophenone with the *n*-Alkanes: A Model for Bimolecular Reactions of Polymers

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ABSTRACT: The photochemical reaction between benzophenone and the *n*-alkanes has been examined. Rate constants have been obtained as a function of temperature for hexane through hexatriacontane. These show parallel Arrhenius plots with $E_a = 3.9 \pm 0.2$ kcal/mol for all chain lengths. At room temperature, the second-order rate constants increase linearly with chain length with a slope of 0.94×10^4 M^{-1} s^{-1} per CH_2 group. A model is proposed to account for this behavior.

Outside of enzyme kinetics, there have not been many kinetic studies of the reaction of small molecules with dilute solutions of polymers. Such studies are important in that they examine the consequence of the non-uniform distribution of reactants in solution. For example, imagine a polymer chain containing noninteracting catalytic groups along its backbone. A solution containing small amounts of this polymer would have regions of relatively high concentration of catalytic groups surrounded by regions containing no such groups. It is important to understand the way in which small molecules would react with such a polymer, if only to be able to use such knowledge to infer cooperative catalysis when appropriate deviations from this behavior were found.

There should be two limiting cases in such reactions. In the diffusion-limited case studied by Schnabel and his co-workers,[1,2] the rate of the reaction is limited by the diffusion of the reactive species into the region of space containing the polymer. Here it is effectively swallowed up by chemical reaction. An example is the reaction of ·OH generated by pulse radiolysis with poly(ethylene oxide) where $\sim OCH_2\dot{C}HO\sim$ refers to the site of the polymer from which a hydrogen atom was abstracted by ·OH. The molar second-order rate constant for this reaction increased as (mol wt)$^{0.6}$, consistent with a simple diffusion model in which the rate increased in proportion to the radius of polymer presented to the approaching ·OH reactant.

$$HO\cdot + HO(CH_2CH_2O)_xH \xrightarrow[H_2O]{} H_2O + \sim OCH_2\dot{C}HO\sim \quad (1)$$

In the other limit, the polymer and reactant encounter each other many times before reacting. Since the rate of the reaction is not limited by the rate of diffusion of the reactants together, the measured rate will be sensitive to other aspects of their interaction. These may include not only the details of bond breaking and bond making in the transition state of the reaction but perhaps other features as well, such as polymer chain length and conformation.

To examine these features, one should choose a reaction for kinetic studies that satisfies a number of important criteria: (i) The reaction should be much slower than diffusion controlled (i.e., the second-order rate constant should be less than 10^7–10^8 M^{-1} s^{-1}); (ii) the polymer should be capable of reacting at many sites along its backbone; but (iii) under the conditions of the kinetic study, no polymer should react more than once. In addition, the studies should be carried out at dilutions sufficient that no polymer–polymer interpenetration occurs. Among the examples of such reactions are those of polyethylene or poly(ethylene oxide) with hydrogen abstracting species much less reactive than ·OH, e.g., *tert*-butoxy radical or excited states of aromatic ketones.

Several years ago we reported preliminary results on the kinetics of reaction of photoexcited benzophenone with dilute solutions of the *n*-alkanes.[3] A peculiar saturation effect was observed such that for long chain alkanes, the second-order rate constant appeared to level off as the chain got longer. After many unsuccessful attempts to develop models that would explain this behavior, we began to question our original data. We have repeated our original measurements, extended our study to longer chain lengths, and examined the temperature dependence of the reaction between the *n*-alkanes and photoexcited benzophenone. Some of our original data were in error.[3] The saturation effect does not exist. The bimolecular rate constant for this reaction increases linearly with chain

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length. The results presented below provide a simple and coherent picture of how small molecules react with polymers in dilute solution.

Experimental Section

Alkanes were purchased from Aldrich Chemical Corp. or Chemical Samples Co. Crystalline alkanes were recrystallized from CCl_4 containing 1% bromine and twice subsequently from CCl_4. They were then sublimed under vacuum. Liquid alkanes were stirred under nitrogen with successive portions of concentrated H_2SO_4 until the sulfuric acid layer remained clear. After the alkane was washed with water and sodium bicarbonate solution, it was dried over magnesium sulfate and distilled. Benzophenone was recrystallized three times from ethanol and then sublimed.

Carbon tetrachloride (spectro grade, glass distilled, Burdick and Jackson) was further purified by irradiating 4 L containing 1 g of benzophenone with light of $\lambda > 300$ nm for 24 h. After the solution was distilled, an additional gram of benzophenone was added, and the solution was reirradiated. The CCl_4 was distilled and then carefully fractionally distilled through a 24 in. Vigreux column. The middle 80% was used in these studies.

Samples containing 1.0×10^{-3} M benzophenone and alkane concentrations varying from 1×10^{-3} to 5×10^{-2} M were prepared. The range of concentrations differed for each alkane but was chosen so that the highest concentration quenched 90% of the benzophenone phosphorescence. Pyrex tubes of 13 mm o.d. containing 3.0 mL of these solutions were attached to an all glass, mercury-free, high-vacuum line and degassed by five successive freeze–pump–thaw cycles. After the fifth cycle, the pressure above the frozen sample was less than 1×10^{-5} torr. The samples were sealed under vacuum and stored in the dark.

For each alkane, samples were prepared containing five different alkane concentrations. These plus a sample containing benzophenone but no alkane, simultaneously prepared, were placed in a rotating aluminum block through which a water–ethylene glycol mixture was pumped from a Lauda K4R or K2R constant temperature bath. Once the block reached a stable temperature, an electric motor allowed each sample in turn to be rotated into the optical path of the flash lamp.

Light flashes were provided by a Xenon Corp. Nanopulser air-spark lamp which produced 50 000-W white light discharges with a time width at half intensity of ca. 30 ns. This light was focused onto the sample after it passed through two Corning 7-60 blue filters to remove the visible component ($\lambda > 390$ nm) of the light. Emitted light from the sample was collected, passed through a liquid filter of 1 M *o*-hydroxybenzophenone in toluene and a Schott low fluorescence 405-nm long pass filter, and focused on a Hammamatsu R212UH (high-sensitivity selected 1P28 type) photomultiplier tube. The phototube output passed through an operational amplifier and across a resistor chosen to provide optimum voltage at the expense of the RC time constant of the circuitry. RC time constants were almost always a factor of 10 less than the measured emissive decay times.

The output of the circuitry was fed to a Biomation 8100 transient waveform recorder, where the signal was digitized and transferred, channel for channel, to a Nuclear Data 1100 multichannel analyzer. Repetitive signals were added giving an improvement in signal-to-noise proportional to the square root of the number of flashes averaged. The intensity vs. time data were punched onto paper tape and fitted by computer using a nonlinear least-squares algorithm.

Typically 1 to 5 decay traces were averaged to obtain each lifetime. Duplicate sets of samples were usually prepared. One was examined in order of increasing, the other in order of decreasing, temperatures. With two important exceptions, room temperature (21 °C) values of the second-order rate coefficients calculated from eq 2 for those alkanes previously studied were virtually identical with those reported previously.

Results and Discussion

Upon absorption of a photon, benzophenone is excited to a singlet electronically excited state from which it decays to its lowest $n\pi^*$ triplet state with 100% efficiency in about 10 ps.[4] This triplet state is long lived. In the absence of something with which it can react, the triplet state persists for 80 to 200 μs. These are typical lifetimes for "nonreactive" solvents like CCl_4, fluorocarbons, acetonitrile, and acetic acid, and the exact lifetime depends upon the purity of the solvent or upon the rate of the slow reaction between the triplet state and the solvent molecules. In competition with this radiationless decay, benzophenone triplets emit light (phosphoresce). The time decay profile of this emission, after a pulse of exciting light, is the means of determining the excited state lifetime τ. This lifetime τ is defined as the time necessary for the intensity to decay to $1/e$ of its initial value.

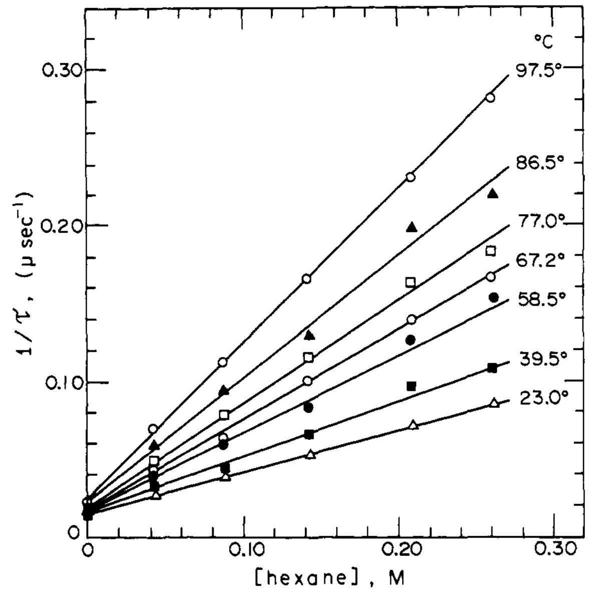


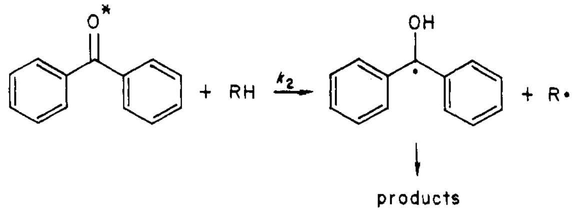
Figure 1. Plot of reciprocal measured lifetimes for benzophenone phosphorescence in CCl_4 in the presence of various concentrations of *n*-hexane, at the temperatures indicated.

In the presence of reactants, the chemical reactions shorten the lifetime of the excited state.[4] Increasing amounts of reactant induce further decreases in τ. Mathematically, the dependence of the measured lifetime upon the reactant concentration [RH] is expressed by the Stern–Volmer equation, where τ^0 is the excited state

$$\frac{1}{\tau} = \frac{1}{\tau^0} + k_2[\mathrm{RH}] \qquad (2)$$

lifetime in the absence of reactant RH and k_2 is the second-order rate coefficient for the reaction. With alkanes, the excited state of ketones undergoes hydrogen abstraction reactions to give radicals which then combine to give a variety of products.[5] By monitoring emission of light from the ketone excited state, one measures only what occurs in the first step of the reaction—the indiscriminate abstraction of a hydrogen from one of many identically reactive CH bonds in the alkane.

The reaction of alkanes with excited benzophenone has been studied in detail.[4,5] Equation 2 is followed without exception for low molecular weight alkanes, and our data satisfied eq 2 for all the *n*-alkanes we examined (Figure 1). A plot of k_2 vs. alkane chain length is presented in Figure 2, and the numerical data are collected in Table I.



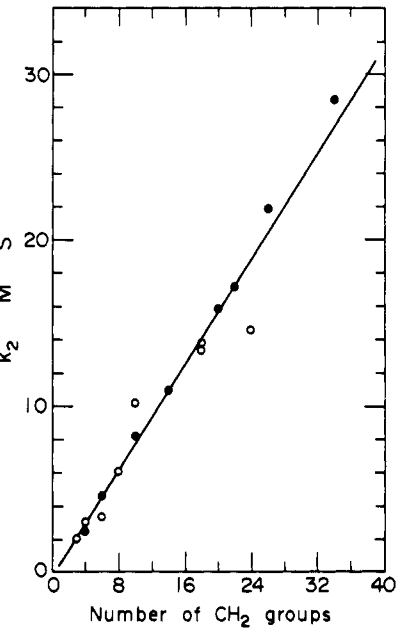


Figure 2. Plot of the second-order rate constants for reaction of benzophenone triplets with the *n*-alkanes $CH_3(CH_2)_{n-2}CH_3$ at room temperature. Open circles are data from ref 3. Those data (ref 3) for dodecane and hexacosane were in error.

Table I
Rate Constants, Arrhenius Activation Energies (E_a), Activation Enthalpies ($\Delta H^{\ddagger}$), and Activation Entropies for the Reaction of Benzophenone Triplets with *n*-Alkanes $CH_3(CH_2)_{n-2}CH_3$ in Carbon Tetrachlorides[a,b]

n	$10^{-8}A$, m^{-1} s^{-1}	E_a, kcal/mol	$10^{-5}k_2^{20}$, M^{-1} s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
6	2.17	3.94	2.55	3.29	22.6
8	4.05	3.95	4.65	3.29	21.4
12	8.62	4.10	8.24	3.43	19.9
16	9.70	3.97	10.9	3.31	19.6
22	11.4	3.84	15.8	3.19	19.3
24	9.74	3.69	17.2	3.04	19.6
28	15.6	3.82	22.1	3.19	18.6
36	20.7	3.84	28.7	3.18	18.1
		av (3.89)			

[a] Rate constants are corrected for solvent density changes at each temperature (J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds", Vol. II, Elsevier, New York, 1965, pp 184 and 434). [b] $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are obtained from plots of $\ln(k_q/T)$ vs. $(1/T)$.

This second-order rate constant increases linearly with chain length for chains up to 36 carbons.

Steel and his co-workers[6] have examined the temperature dependence of k_2 for several simple alkanes in acetonitrile solution. His studies indicate that k_2 increases with temperature in a manner consistent with a small energy barrier to the excited state reaction. From Arrhenius plots he has found activation energies E_a of ~4 kcal/mol for primary CH bonds, ~3 kcal/mol for secondary CH bonds, and ~2 kcal/mol for tertiary CH bonds.

We measured phosphorescence lifetimes of benzophenone–alkane solutions in CCl_4 at a series of temperatures between 0 and 100 °C. Values of k_2 obtained from the Stern–Volmer equation are plotted according to the Arrhenius equation in Figure 3. The series of parallel lines indicates that the activation energies for each of the *n*-alkanes toward hydrogen abstraction are identical. We calculate a value of 3.9 ± 0.2 kcal/mol for E_a.

Factors Controlling the Dependence of k_2 upon Chain Length. From the slope of the line in Figure 2, one can calculate a room-temperature rate constant of 0.94×10^4 M^{-1} s^{-1} per CH_2 group for the reaction of *n*-alkanes with photoexcited benzophenone. This linear dependence of k_2 on n has some interesting consequences. It suggests, for example, that if one were to cut in half all the polymer chains in a reaction vessel, the *rate* of the chemical reaction would remain unchanged. The rate constant for the reaction would be halved, but the concentration of polymer would double. This is consistent with the entropic origin of the increase in k_2 with chain length. For bimolecular reactions, activation entropies are a function of concentration, and standard entropies are obtained by reference to a standard state (1 M solution).

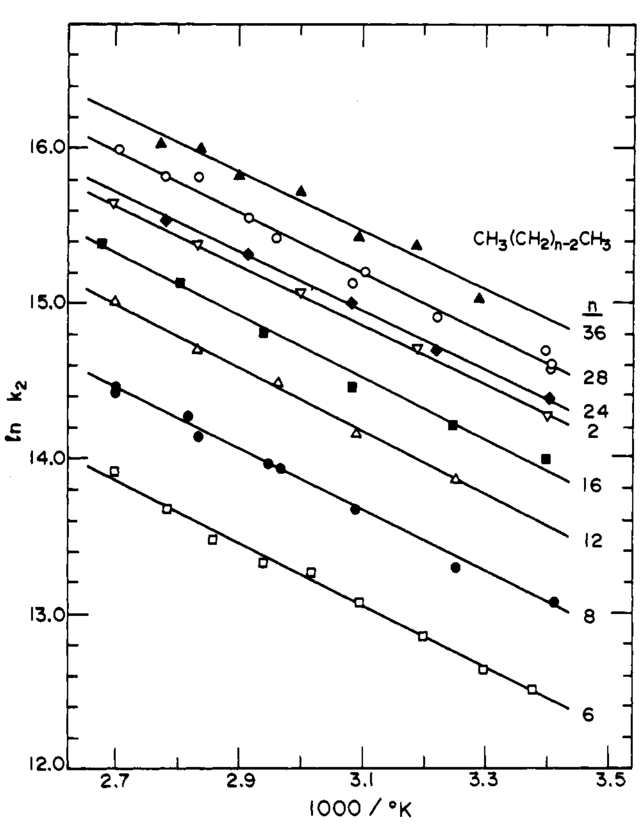


Figure 3. Arrhenius plots of ln k_2 vs. $1000/T$ for the reactions of the *n*-alkanes with photoexcited benzophenone. The chain length in $CH_3(CH_2)_{n-2}CH_3$ is indicated along the right-hand ordinate.

In the extreme case, our results suggest that one would observe no difference in reaction rate if one were examining one polymer molecule of x segments or n molecules, each made up of x/n segments. Thus our results indicate that the reaction rate depends only upon the *total* concentration of monomer units in solution. It appears not to depend upon whether they are distributed uniformly in solution or upon the conformation of the polymer they compose.

One can construct a simple model of polymer reactivity that leads to the same conclusion.[7] To do this, one must recognize that while the polymer has its segments S concentrated in certain regions of space, the benzophenone excited state B* is uniformly distributed. Consider dividing the solution up into many small compartments. In the case where S represents individual segments free in solution, one can write the rate of reaction as

$$-d[B^*]/dt = k_2'[B^*][S] \qquad (3)$$

where [B*] and [S] represent the uniform concentration of B* and S, respectively, in each of the compartments. k_2' is the per-segment second-order rate constant for the reaction.

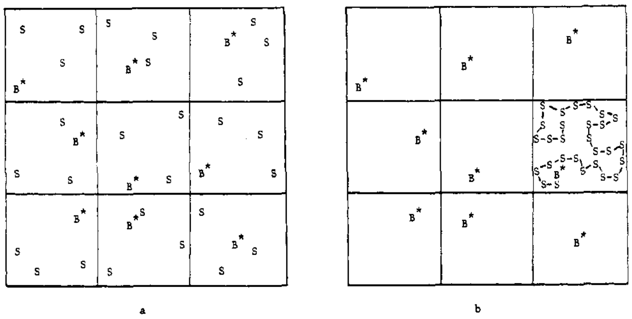


Figure 4. Pictorial representation of the reaction between B* and S when individual S units are free in solution (a) and connected to form a polymer chain (b). If this reaction is sufficiently slow that the B* molecules equilibrate between the boxes before the reaction occurs, both "solutions" will show the same macroscopic kinetics. This will no longer be true in the case of a diffusion-controlled reaction.

In the case where the segments are joined into a polymer, the concentration of S in the *j*th compartment is $[S_j]$. For a fixed sufficiently dilute solution, $[S_j]$ will be zero in most compartments. The number of compartments having nonzero values of $[S_j]$ and the magnitude of $[S_j]$ will depend upon the degree of polymerization. From a macroscopic point of view, the observed rate will be the average rate of reaction over all J compartments.

$$-\frac{d[B^*]}{dt} = \frac{1}{J}\sum_{j=1}^{J} k_2'[B^*][S_j] \qquad (4)$$

$[B^*]$ is uniform in solution, and k_2' is independent of chain length. The two reaction rates are the same since $(1/J)\sum[S_j] = [S]$.

This point is easily illustrated in terms of the nine-box grid shown in Figure 4. In Figure 4a the reactants B* and S are uniformly distributed. Their reaction rate is described by eq 3. In Figure 4b, all the S molecules are located in one box. In that box, B* reacts nine times as fast. The macroscopic rate is the average rate in all nine boxes and is identical with that in Figure 4a.

For a chemical reaction to show this behavior, k_2' or k_2 must be smaller than the diffusion limit. Otherwise, the concentration of B* in the compartments containing polymer would diminish faster than in other compartments. The assumption of uniform distribution presumes fast exchange between compartments and is substantiated experimentally by the observation of single exponential decays for excited benzophenone at all alkane concentrations.

The straight line in Figure 2 suggests that the second-order molar rate constant for the reaction increases without limit for high polymers. Alkanes are not the best substrates for testing this prediction because of their poor solubility. Whether such behavior continues for chains of 100 or 10^4 atoms would be very interesting to establish.

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Substituent Effects on Hydrocarbon Chain Cyclization Probed by an Intramolecular Photochemical Reaction

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ABSTRACT: The molecules benzophenone-4-$CO_2(CH_2)_nCH_3$(IV) undergo an intramolecular hydrogen abstraction reaction. So, too, do the molecules benzophenone-4-CO_2-X′-$O_2C(CH_2)_{12}CH_3$, where the substituents (I, X′ = $-CH_2CH_2-$, II, X′ = *trans*-1,2-cyclohexyl, and III, X′ = 1,2-benzenyl) impose conformational constraints on the chain which are predicted to increase the cyclization probability of the chain. Flash photolysis measurements indicate that cyclization is enhanced by factors of 2.5, 6, and 9 for I, II, and III, respectively, over the 17-carbon ester of IV.

Introducing a substituent into a flexible chain molecule affects the conformation of the chain.[1] In hydrocarbon chains, a small substituent might affect only the gauche/trans rotational populations of nearly C–C bonds. Larger substituents can cause rotational angle distortion and other effects which are extremely difficult to describe, much less to quantify. Since the overall problem is complex, individual examples where the effect of a single substituent on the conformation of a hydrocarbon chain can be assessed serve as a valuable guide to our understanding of substituent effects on chain properties.

The molecules I, II, and III[2] contain substituents on sites corresponding to the 1, 2, 3, and 4 positions (see Scheme I) of the hydrocarbon chain of the parent molecule IV-17.

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