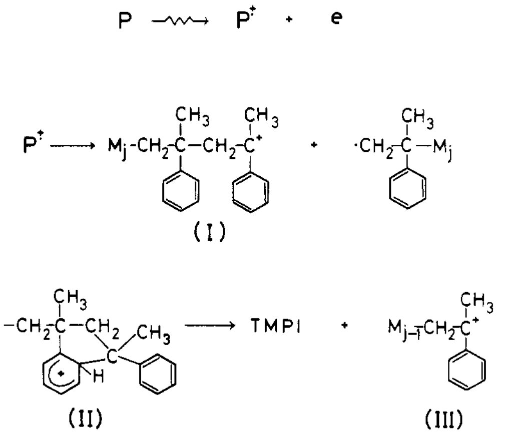
TMPI is known to be formed in the acid-catalyzed dimerization of α-methylstyrene together with linear dimers.[3] It has also been reported that in the cationic polymerization of α-methylstyrene by catalyst a 1,3-dimethyl-3-phenylindanyl end group is formed by the electrophilic substitution of the penultimate benzene ring by the propagating cation.[4] These facts suggest that the dimer is formed by the reaction of the carbonium ion produced by irradiation.

Usually, in the radiolysis of hydrocarbons the effect of the addition of a cation scavenger such as ammonia, alcohol, or ether on product yields is examined in order to obtain evidence for the cationic processes of product formations. In the present investigation poly(isobutyl vinyl ether) was used as a cation scavenger because any volatile additive is not suitable for the reaction at high temperature under vacuum. The yield of the dimer was reduced to less than one-third by the addition of about 3 wt % of poly(isobutyl vinyl ether).[5] The incomplete inhibition of the dimer formation is probably due to the low mobility of the reaction sites in the solid polymer. Thus, it can be concluded that the dimer is formed via a cationic process. The proposed mechanism is as follows:



where P and M denote a polymer chain and a monomer unit, respectively. The stable tertiary carbonium ion (I) is produced from the polymer cation, $P\cdot^{+}$, and the chain end cyclizes by the carbonium ion substituting the penultimate phenyl ring to give II analogously to the propagating chain end in the cationic polymerization.[4] The carbonium ion III produced by the last step again yields the dimer similarly to I.

The last step of the scheme, which is regarded as an intramolecular protolysis of the C– bond by the proton derived from the aromatic ring, should require a high activation energy. The protolysis of a C–C bond has recently been reported in the study using superacid.[6] The result of the present study seems to suggest that at high temperature the protolysis of the weak C–C bond generating the stable tertiary carbonium ion occurs by such a weak acid as the benzenium ion.[7]

Cationic chain reactions occurring in the radiation-induced pyrolysis have been reported in the ether formations from alcohols[8] and the decomposition of *n*-butane.[9] The dimer formation from poly(α-methylstyrene) should be one of the examples of such ionic chain reactions occurring at high temperature.

Acknowledgment. We wish to thank Drs. Hitoshi Yamaoka and Tomiki Ikeda of Kyoto University for their helpful discussions.

References and Notes

(1) (a) H. H. G. Jellinek, *J. Polym. Sci.*, **4**, 13 (1949); (b) S. L. Madorsky, *ibid.*, **9**, 133 (1952); **11**, 491 (1953); (c) D. W. Brown and L. A. Wall, *J. Phys. Chem.*, **62**, 848 (1958); (d) J. M. G. Cowie and S. Bywater, *J. Polym. Sci.*, **54**, 221 (1961); (e) H. H. G. Jellinek and H. Kachi, *J. Polym. Sci., Part C*, **23**, 97 (1968).

(2) The polymer used in the experiment was obtained by the radiation-induced polymerization in bulk under extensively dry conditions. It was precipitated by an excess of methanol, filtered, and dried in a vacuum oven. The degree of polymerization was 2.1×10^2.

(3) S. Bywater, "The Chemistry of Cationic Polymerization", P. H. Plesch, Pergamon Press, New York, N. Y., 1963.

(4) F. S. Dainton and R. H. Tomlinson, *J. Chem. Soc.*, 151 (1953).

(5) The poly(α-methylstyrene) powder containing a small amount of poly(isobutyl vinyl ether) was prepared by the freeze-dry method from the dilute benzene solution.

(6) (a) G. A. Olah, G. Klopman, and R. H. Schlosberg, *J. Am. Chem. Soc.*, **91**, 3261 (1969); (b) G. A. Olah, Y. Halpern, J. Shen, and Y. K. Mo, *ibid.*, **93**, 1251 (1971).

(7) In the radiation-induced pyrolysis of polystyrene under the same condition as that in the case of poly(α-methylstyrene), 1-methyl-1-phenylindane was not produced in a detectable amount, indicating that the chain reaction is not initiated when the intermediate cation is the less stable secondary carbonium ion.

(8) K. M. Bansal and G. R. Freeman, *J. Am. Chem. Soc.*, **90**, 5632 (1968); **92**, 4173, 4417 (1970).

(9) S. Matsuoka, T. Tamura, K. Oshima, and Y. Oshima, *Can. J. Chem.*, **53**, 92 (1975).

Yukio Yamamoto,* Miyako Himei, and Koichiro Hayashi
The Institute of Scientific and Industrial Research,
Osaka University, Suita, Osaka, Japan
Received June 16, 1976

Phosphorescence Quenching in the Photoreaction of Benzophenone with the *n*-Alkanes. A Model for the Interaction of Small Molecules with Polymers

When a small molecule reacts with a polymer, the kinetics of that reaction can reveal details of the interaction between the two species. In enzyme kinetics, the apparent binding constant of a substrate to the active site can be inferred from a proper treatment of the rate data.[1] In the reaction of ·OH radicals with various polymers, the *chain length dependence* of the second order rate constant has been related to the chain length dependence of the end-to-end distance of the polymer.[2] When the small molecule is sufficiently reactive that it reacts with the polymer on virtually every collision, the corresponding second order rate constant is sensitive primarily to the shape of the polymer.[2] If the small molecule is sufficiently unreactive that it reacts only once every 1000 or more collisions, other facets of the polymer–small molecule interaction are probed.

In this paper we present results of a kinetic study of the reaction between photoexcited benzophenone and a series of *n*-alkanes, examined in dilute carbon tetrachloride solution. Values of the second order rate constants $k_{\mathrm{obsd}}(n)$ are reported as a function of the alkane chain length. These values provide a unique insight into the nature of encounter complexes involving randomly coiled alkane polymers.

The power of this reaction to provide a glimpse at details of a polymer–small molecule interaction derives from three facets of hydrogen abstraction reactions: (a) each of the CH_2 groups in the alkanes are equally reactive toward benzophenone triplets;[3] (b) the methyl groups are relatively unreactive; and (c) rate constants for reaction of benzophenone triplets with alkanes are four orders of magnitude slower than the diffusion limit. These factors permit the excited benzophenone (i) to undergo collisions with thousands of alkane molecules before reacting and (ii) to encounter many CH_2 groups in an alkane within one collision complex. The latter factor leads to the prediction that the second order rate constant should increase with increasing chain length of the alkane "polymer".

Benzophenone triplets react with alkanes by hydrogen abstraction to yield a pair of radicals. This reaction is closely related to hydrogen abstraction reactions of *tert*-butyl-O·, Cl·,

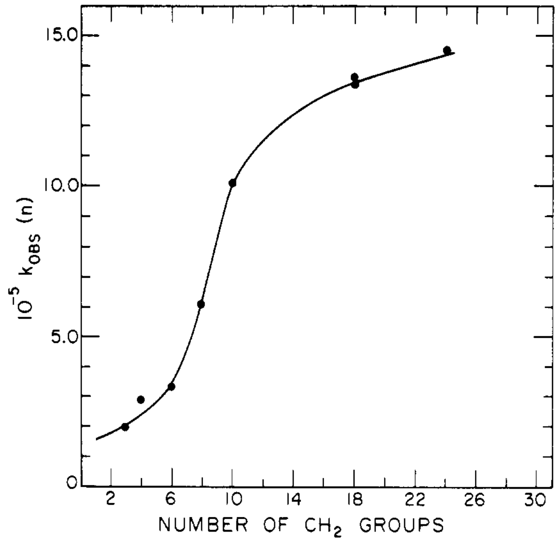


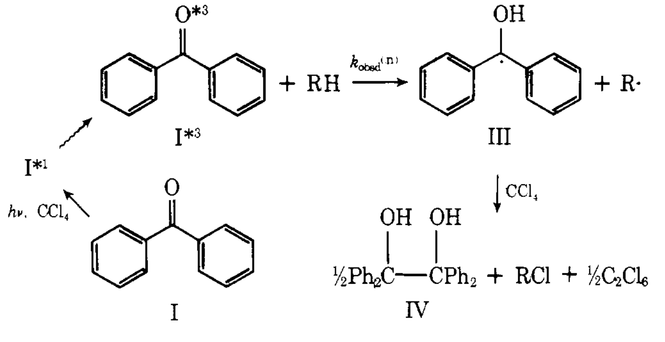
Figure 1. Plot of the second order rate constant $k_{obsd}(n)$ vs. n for the reaction of benzophenone in its excited triplet state with $CH_3(CH_2)_nCH_3$. The two points for n = 18 refer to experiments with samples of n-eicosane purified by two different methods.

and HO·, each giving products typical of radical processes.[4] These reactions are all of the form

$$RH + B\cdot \xrightarrow{k_{obsd}} R\cdot + HB$$

If RH is an n-alkane, one might expect that k_{obsd} would increase with the number of methylenes in the alkane. The details of the dependence of k_{obsd} on n are difficult to predict. These details hold the key to insights into the nature of the encounter complex between the reactant and the alkane polymer.

Scheme I



In the case reported here, the alkyl radicals are trapped by reaction with solvent. The ·CCl_3 radicals and the ketyl radicals III selectively dimerize[5] [Scheme I]. These reactions are clean[5,6] and rather well understood from a kinetic point of view.[5-7] Benzophenone photoreactions are particularly attractive for probing alkane–small molecule interactions. Values of $k_{obsd}(n)$ are easily obtained with high precision (better than ±5%) from flash photolysis experiments.[7,8]

We have examined the interaction of benzophenone, in its excited triplet state, with a series of n-alkanes, from pentane to hexacosane. For each alkane, six sample tubes were prepared. All contained 1×10^{-3} M benzophenone in carbon tetrachloride, and five contained various concentrations of the alkane. Alkane concentrations covered the range 5×10^{-4} to 1×10^{-2} M. For any one alkane, five samples spanned an order of magnitude in concentration.[13] The sample tubes were rigorously outgassed[8] on a vacuum line and sealed. Triplet lifetimes τ were obtained by flash emission studies.[8] Decays were exponential. Lifetimes were obtained by fitting the decay traces nonlinearly. Precision in τ measurements was typically ±3-4%.

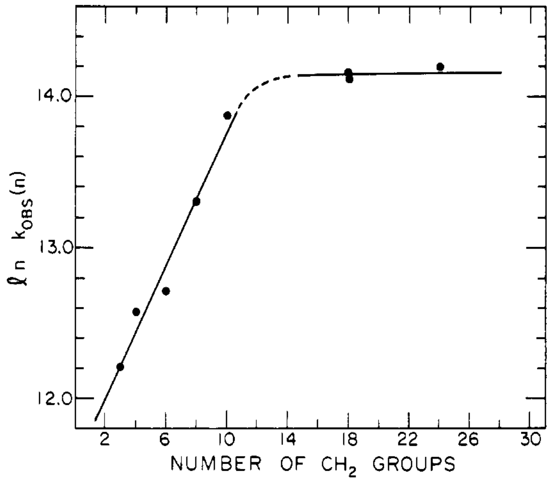


Figure 2. Plot of ln $k_{obsd}(n)$ vs. n for the reaction of benzophenone in its excited triplet state with $CH_3(CH_2)_nCH_3$.

$$\frac{1}{\tau} = \frac{1}{\tau_0} + k_{obsd}(n)[RH] \qquad (1)$$

Second order rate constants, $k_{obsd}(n)$, were obtained by fitting the data to the Stern–Volmer equation (eq 1), where τ_0 is the triplet lifetime in the absence of alkane quencher. These plots were strictly linear. They gave excellent correlation coefficients (>0.98), and standard deviations in the slope were never more than ±5%. Values of $k_{obsd}(n)$ were insensitive to large changes in benzophenone concentration; duplicate determinations of $k_{obsd}(n)$ always gave values within ±5%. It is important to note that the rate "constants" $k_{obsd}(n)$ are phenomenologic constants defined by d[excited state]/dt = $-k_{obsd}(n)[I^{*3}][RH]$.

Values for $k_{obsd}(n)$ are presented in Figure 1 as a function of n. These values are extremely sensitive to the presence of olefinic impurities in the alkanes and very careful precautions were taken to ensure their purity. Standard techniques suffice for purifying liquid samples of the n-alkanes.[7,8] We developed new methods for solid samples of alkanes. For n-eicosane, where both methods could be used, $k_{obsd}(n)$ values agreed within 3%. Impurities can cause $k_{obsd}(n)$ values to be too large. Thus n-eicosane, partially purified by repeated crystallization and sublimation, gave a $k_{obsd}(n)$ value too high by 10%.

Many aspects of Figure 1 are surprising. First of all, at short chain lengths, $k_{obsd}(n)$ increases faster than the number of CH_2 groups. A plot of ln $K_{obsd}(n)$ vs. n is linear (Figure 2) suggesting that $k_{obsd}(n)$ increases exponentially rather than linearly with n. Second, for sufficiently long chains, $k_{obsd}(n)$ abruptly begins to level off. The sigmoidal nature of the curve of Figure 1 is most disturbing. A titration-like curve implies a saturation effect; it is not immediately apparent what, in the interaction of benzophenone and the alkane polymer, is saturating.

We base our interpretation of these results on recent evidence that hydrocarbon chains are randomly oriented in dilute solution in carbon tetrachloride.[9] We specifically ignore aggregation, which has been inferred for concentrated solutions.[10] More peculiar explanations which require severe deviations from ideal solution behavior (like hairpin configurations[11]) are not applicable here.

North[12] has treated the kinetics of the interaction of two reactive polymers each containing a reactive functional group. This treatment can be applied to the interaction of a small molecule with a polymer. North envisions the encounter phenomena as three consecutive processes. These are: (a) diffusion together of the two reactants from some random position in solution so that they are no longer separated by a solvent molecule; (b) rearrangement or rotation of the macromolecular encounter pair so that the reactive portions of the molecules collide and so that these groups are correctly oriented for chemical reaction to take place; and (c) chemical reaction of the active groups. These three stages can be represented in a kinetic scheme as

$$\mathrm{A} + \mathrm{B} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (\cdot\mathrm{AB}\cdot) \qquad (2)$$

$$(\cdot\mathrm{AB}\cdot) \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} (\mathrm{A}\cdot\cdot\mathrm{B}) \qquad (3)$$

$$(\mathrm{A}\cdot\cdot\mathrm{B}) \xrightarrow{k_c} \qquad (4)$$

(·AB·) represents macromolecular encounter pairs with the reactive groups in positions which are unfavorable for chemical reaction and (A· ·B) represents those with the groups favorably oriented for reaction. We will call the former kind of encounter pairs "unreactive complexes" and the latter "reactive complexes" and note that there need not be an enthalpy of binding in the complexes beyond that holding molecules together in a solvent cage.

Equations 2–4 predict that k_{obsd} is described by eq 5 when the chemical reaction is much slower both than diffusion controlled ($k_{\mathrm{obsd}} \ll k_1$) and molecular reorientation ($k_c \ll k_{-2}$). The terms $K_1 = k_1/k_{-1}$ and $K_2 = k_2/k_{-2}$ represent the equilibrium constants for formation of the two kinds of intermediate pairs.

$$k_{\mathrm{obsd}} = K_1 K_2 k_c \qquad (5)$$

In the reaction of an alkane with benzophenone in its excited state, there are many reactive and unreactive conformations within the encounter pair. If the results we observe depend upon the equilibrium between reactive and unreactive conformations, then the interesting features of the mechanism would be contained in the K_2 term in eq 5. This presumes that the encounter pair reaches the equilibrium described by K_2. In fact the situation is more complicated. This equilibrium may be reached when the chain is short. One would then expect that K_2 would increase with increasing n, and the fraction of reactive conformations would increase as the number of $\mathrm{CH_2}$ groups increases. For long chains, equilibrium is not established. The lifetime of an encounter pair is limited by the rate at which the two species diffuse apart. There is not sufficient time, within one encounter complex, for the excited benzophenone and the alkane to sample all possible reactive and unreactive configurations. Under these conditions, the assumptions necessary to derive (5) no longer hold.

We propose a *dynamic* aspect to the reactant–polymer interaction to explain the curve shapes in Figures 1 and 2. We attribute the leveling of the curves in Figures 1 and 2 at large n to limitations in the number of $\mathrm{CH_2}$ groups which the excited benzophenone can visit during the lifetime of an encounter complex. Only a fraction of the reactive configurations contribute to the magnitude of $k_{\mathrm{obsd}}(n)$ because the rate of diffusion out of the encounter pair is competitive with the rate of conformational change within the encounter pair. The rate constant k_{-1} acts as a clock: $k_{-1}{}^{-1}$ determines the lifetime of the encounter complex; it limits the number of reactive sites and reactive conformations accessible to the reactants within an encounter pair. Since hydrogen abstraction is very slow relative to the rates of rotation and molecular diffusion, the triplet state of benzophenone must be involved in thousands of different encounter complexes during its (many microsecond) lifetime. On a time average, all reactive and unreactive configurations of the polymer–reactant pairs will be visited.

While the change from equilibrium control to dynamic control explains the rapid increase in $k_{\mathrm{obsd}}(n)$ at low n, and at large n its subsequent leveling off, this explanation is not complete. Some clearly important factors have been ignored and features of the reaction remain unexplained. The diffusion constants, for example, of the alkanes change significantly for these values of n, affecting both the lifetimes of the encounter pairs and the number of complexes experienced by each excited benzophenone. The relative insensitivity of benzophenone triplets to changes from chains of 5 to 8 carbons suggests that more factors are involved than just the number of $\mathrm{CH_2}$ groups. Details of the geometry of the encounter pair, and the accessibility of conformers with the unreactive methyl groups away from the ketone oxygen, must play an important role in determining the magnitude of $k_{\mathrm{obsd}}(n)$.

Modeling the dynamic competition, in mathematical terms, between k_{-1} and the rate constant for conformational change in the encounter complex is very difficult. Efforts to that end are underway.

In summary, it appears that when benzophenone interacts with an alkane polymer, the lifetime of the interaction is determined by the rate of diffusion away from the encounter pair. Within the encounter complex, benzophenone triplets can, on the average, come in contact with approximately 14 $\mathrm{CH_2}$ groups.

Acknowledgment. We appreciate the financial support of the National Research Council of Canada and Research Corporation. We would like to thank Professors J. E. Guillet, S. G. Whittington, M. Moskovits, J. Deckers, and Ms. J. C. Poë for their patient, critical comments, their insights and suggestions, and their wit and good humor, as we struggled to make sense of our experimental results. In addition we would like to thank Professors A. M. North and H. Morawetz for reading the manuscript and making several important suggestions.

References and Notes

(1) J. Steinhardt and J. A. Reynolds, "Multiple Equilibria in Proteins", Academic Press, New York, N.Y., 1969.

(2) (a) Behzadi and W. Schnabel, *Macromolecules*, **6**, 824 (1973); (b) A. Behzadi, U. Borgwardt, A. Henglein, E. Schamberg, and W. Schnabie, *Ber. Bunsenges. Phys. Chem.*, **74**, 649 (1970); (c) M. Anbar, D. Meyerstein, and P. Neta, *J. Chem. Soc. B*, 742 (1966).

(3) (a) P. Smit and H. J. den Hertog, *Recl. Trav. Chim. Pays-Bas*, **83**, 891 (1964); (b) N. C. Deno, R. Fishbein, and C. Pierson, *J. Am. Chem. Soc.*, **92**, 1451 (1970).

(4) C. Walling "Free Radicals in Solution", Wiley, New York, N.Y., 1957.

(5) (a) C. Walling and M. J. Gibian, *J. Am. Chem. Soc.*, **87**, 3361 (1965); (b) **86**, 3902 (1964).

(6) (a) J. Chilton, L. Giering, and C. Steel, *J. Am. Chem. Soc.*, **98**, 1865 (1976); (b) M. R. Topp, *Chem. Phys. Lett.*, **32**, 144 (1975).

(7) L. Giering, M. Berger, and C. Steel, *J. Am. Chem. Soc.*, **96**, 953 (1974).

(8) M. A. Winnik, C. K. Lee, S. Basu, and D. S. Saunders, *J. Am. Chem. Soc.*, **98**, 2928 (1976).

(9) (a) M. A. Winnik, A. Lemire, D. S. Saunders, and C. K. Lee, *J. Am. Chem. Soc.*, **98**, 2000 (1976); (b) M. A. Winnik, C. K. Lee, S. N. Basu, and D. S. Saunders, *ibid.*, **96**, 6182 (1974); (c) G. D. Patterson and P. J. Flory, *J. Chem. Soc., Faraday Trans. 2*, **68**, 1098 (1972).

(10) G. W. Brady, *Acc. Chem. Res.*, **7**, 174 (1974).

(11) K. Liu, *J. Polym. Sci., Part A-2*, **5**, 1209 (1967).

(12) A. M. North "The Collision Theory of Chemical Reactions in Liquids", Methuen and Co. Ltd., London, 1964, pp 126–134.

(13) Concentrations of alkane were chosen for experimental convenience, so that measured values of τ were in the range 0.8 to 0.1 τ_0.

Mitchell A. Winnik* and Ebenezer Shum
Lash Miller Laboratories and Erindale College,
Department of Chemistry, University of Toronto,
Toronto, Canada M5S 1A1

Received March 19, 1976