Chemistry of Singlet Oxygen.
XIII. Solvent Effects on the Reaction with Olefins[1]

Christopher S. Foote* and Robert W. Denny

Contribution No. 2681 from the Department of Chemistry,
University of California, Los Angeles, California 90024.

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Abstract: Solvent effects on the product-forming step of the dye-sensitized photooxygenation of 2-methyl-2-pentene have been measured. The variation in β (ratio of the decay rate of singlet oxygen to its rate of reaction) is very small, amounting to less than a factor of four in the solvents studied. No effect of solvent polarity, internal pressure, viscosity, or heavy atoms can be discerned. The results of these studies and those previously reported are consistent with a concerted reaction mechanism involving a six-center transition state, but do not completely exclude a perepoxide intermediate.

As part of a continuing study of the chemistry of singlet oxygen, the solvent effect on the reaction with olefins was needed to provide further information about the transition state. Because dye-sensitized photooxygenations involve several steps and competing reactions, separation of the oxygenation step requires careful kinetic analysis.[2,3] Detailed kinetic studies of the reaction have been carried out by many groups, and the steps which are important under usual conditions (dye sensitizer with reasonably high intersystem crossing efficiency, absence of powerful hydrogen donors, solution in equilibrium with air or oxygen at 1 atm) are as follows[2]

$$\begin{tikzcd}
\text{sens} \arrow[r, "h\nu"'] & {}^1\text{sens} \arrow[r, "\varphi_{\text{isc}}"'] & {}^3\text{sens} \arrow[r, "O_2"'] & {}^1O_2 \arrow[r, "k_2", "A"'] \arrow[d, "k_1"] & AO_2 \\
 & & & {}^3O_2 &
\end{tikzcd}$$

where sens is sensitizer, excited singlet and triplet states are indicated by appropriate superscripts, $^1O_2$ is singlet molecular oxygen (probably $^1\Delta_g$), and A is the acceptor. The term φ_{isc} is the intersystem crossing quantum yield for the sensitizer, and k_1 and k_2 are the rates of decay and reaction with acceptor of singlet oxygen, respectively. Under the above conditions, all ^{3}sens gives $^1O_2$,[2] and the expression for the overall quantum yield of product (φ_{AO_2}) is given by

$$\varphi_{AO_2} = \varphi_{\text{isc}} \frac{k_2[A]}{k_2[A] + k_1}$$

This expression is equivalent to the following, in which I_{abs} is the number of mole quanta per liter absorbed during the irradiation time, and $[AO_2]$ is the final concentration of the product peroxide produced. Plots

$$[AO_2]^{-1} = (I_{\text{abs}}\varphi_{\text{isc}})^{-1}(1 + (k_1/k_2)[A]^{-1})$$

of $[AO_2]^{-1}$ *vs.* $[A]^{-1}$ give straight lines,[3] for which the ratio of the slope to the intercept on the $[AO_2]^{-1}$ axis is k_1/k_2, the ratio of the decay rate of $^1O_2$ to the rate of its reaction with the acceptor, a parameter called β.[2,3] The intercept of such plots is the amount of singlet oxygen formed during the irradiation, and depends on sensitizer and many other factors. The parameter β, however, depends only on acceptor (it is the concentration of acceptor at which half the singlet oxygen is trapped). Thus determination of β for the same acceptor in different solvents is not affected by changes in absorption efficiency or triplet quantum yield of the dye, which in general will change with solvent.[2-4] Of course, it would be desirable to find the solvent effect on k_2 rather than on the ratio k_1/k_2 but no technique for determining absolute values of k_2 has been reported.

Several measurements of solvent effects on β have been reported. Schenck and Gollnick found only a small change in the value of β for citronellol in methanol (0.16 *M*), *n*-butyl alcohol (0.12 *M*), and 70% aqueous methanol (β = 0.06 *M*).[2,7]

Similar small effects on the photooxygenation of 2-methyl-2-pentene were reported in *tert*-butyl alcohol (0.051 *M*) and 50% methanol-*tert*-butyl alcohol (0.13 *M*).[3] In contrast, large effects on β were reported in self-sensitized photooxygenations of anthracene by Bowen,[8] and in chlorophyll-sensitized oxidation of allylthiourea by Livingston and Owens.[9] Consideration of these reports will be deferred until the Discussion.

Results

2-Methyl-2-pentene was chosen as the acceptor for the present studies because previous work had shown that gas-chromatographic analysis of products from this olefin is convenient, and its solubility properties

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(1) Paper XII: C. S. Foote and R. W. Denny, *J. Amer. Chem. Soc.*, **93**, 5162 (1971); supported by National Science Foundation Grant No. GP-5835 and GP-8293; taken in part from R. W. Denny, Ph.D. Thesis, University of California, Los Angeles, 1969.

(2) K. Gollnick, *Advan. Photochem.*, **6**, 1 (1968).

(3) R. Higgins, C. S. Foote, and H. Cheng, *Advan. Chem. Ser.*, No. 77, 102 (1968).

(4) That β is not a function of sensitizer has been documented in many cases (see ref 2 for details). In particular, the β value for 2-methyl-2-pentene is the same with chemically generated singlet oxygen and with Rose Bengal sensitization.[3] The same value is obtained also with methylene blue, zinc tetraphenylporphine, and chlorophylls *a* and *b*, as will be apparent from the results of this study. Relative rates of reaction of several different substrate pairs are also independent of sensitizer.[2,5,6]

(5) K. R. Kopecky and H. J. Reich, *Can. J. Chem.*, **43**, 2265 (1965).

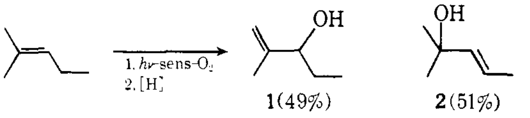
(6) T. Wilson, *J. Amer. Chem. Soc.*, **88**, 2898 (1966).

(7) G. O. Schenck and K. Gollnick, "Forschungsbericht des Landes Nordrhein-Westfalen," Nr. 1256, Westdeutscher Verlag, Köln and Opladen, 1963.

(8) E. J. Bowen, *Discuss. Faraday Soc.*, **14**, 143 (1953); E. J. Bowen, *Advan. Photochem.*, **1**, 23 (1963); E. J. Bowen and D. W. Tanner, *Trans. Faraday Soc.*, **51**, 475 (1955); R. Livingston in "Autoxidation and Antioxidants," W. O. Lundberg, Ed., Vol. I, Wiley-Interscience, New York, N. Y., 1961, p 249.

(9) R. Livingston and K. E. Owens, *J. Amer. Chem. Soc.*, **78**, 3301 (1956).

in various solvents are desirable. Product analysis is more reliable than measurement of acceptor disappearance or oxygen uptake, because side reactions do not interfere.[3] However, because of difficulties in carrying out chemical generation of singlet oxygen in solvents other than alcohol,[10] only the photosensitized oxygenation was studied. The techniques of ref 3 were used, in which solutions containing weighed amounts of acceptor in various solvents and with various sensitizers were photooxygenated for a constant time, then reduced; the product alcohols were determined gas chromatographically, using an internal standard. The ratio of the two products, **1** and **2**, did not change measurably in different solvents from the previously reported[2,3,11] value of roughly 1:1.



A typical plot is shown in Figure 1 for cyclohexanol. The values of β obtained in various solvents (see the Experimental Section for data treatment) are listed in Table I. The standard deviations listed are those for each data set; multiple determinations in several cases showed the values to be generally reproducible to ±20%.

Table I. Value of β (k_1/k_2) for 2-Methyl-2-pentene in Various Solvents at 25°

Solvent	β, M	Std dev	Intercept, M^{-1} ^{j}	Dielectric constant, D, 25°, D	Viscosity, η, 25°, cP
$CH_3CO_2CH_3$^{a}	0.04	0.02	293	6.02	0.44
C_5H_5N^{a}	0.05	0.01	175	12.3	0.97^{g}
C_6H_5Br^{b}	0.05	0.03	177	5.40	0.99^{h}
Cyclohexanol^{a}	0.07	0.01	222	15.5	57
$(CH_3)_2SO$^{a}	0.07	0.01	204	48.9	2.0
$(CH_3)_2CO$^{a}	0.08	0.01	156	20.7	0.32
CS_2^{b,f}	0.08	0.01	330	2.64^{g}	0.36^{g}
C_6H_6^{b}	0.10	0.01	230	2.27	0.65^{g}
C_2H_5I^{b}	0.11	0.03	192	7.56^{h}	0.59^{g}
$C_6H_5OCH_3$^{b}	0.13	0.02	213	4.47^{i}	1.32^{g}
m-$C_6H_4(OCH_3)_2$^{b}	0.15	0.04	2300	5.36	
CH_3OH^{a}	0.16	0.03	140	32.6	0.59^{g}
CH_3OH^{c}	0.13	0.01	k		
CH_3OH^{d}	0.20	0.08	k		
tert-BuOH^{a,l}	0.051	0.003	k	10.9^{h}	5.9
CH_3OH–C_6H_6; 20:80^{e}	0.05	0.005	k		
CH_3OH–*tert*-BuOH; 1:1^{a,l}	0.13	0.02	k		

[a] Rose Bengal sensitizer. [b] Zinc tetraphenylporphine sensitizer. [c] Chlorophyll *b* sensitizer. [d] Chlorophyll *a* sensitizer. [e] Methylene blue sensitizer. Temperature other than 25°. [f] 0°. [g] 20°. [h] 30°. [i] 15°. [j] Corrected to 4-min irradiation if carried out for longer time. [k] Not comparable because run under different conditions of light intensity. [l] Reference 3.

A value for dimethylformamide of 0.03 M was also obtained, but was not considered reliable enough for inclusion in Table I because the analysis was complicated by the presence of products of unknown origin.

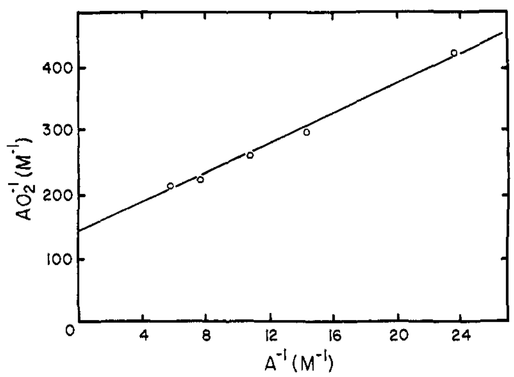


Figure 1. Determination of β for 2-methyl-2-pentene in cyclohexanol.

The values of the intercept of plots of $[AO_2]^{-1}$ *vs.* $[A^{-1}]$ (a measure of the quantum yield of singlet oxygen formation) are also listed in Table I. Because of differences in sensitizer and possible variation in sensitizer concentration, absorption spectrum, and triplet quantum yield with solvent, these values are not expected to remain completely constant. Nevertheless, the variation is small, indicating that the quantum yield of singlet oxygen formation varies only slightly in the different solvents, with the exception of *m*-dimethoxybenzene, for which the intercept is tenfold larger than for the other solvents, which probably indicates substantial quenching of one of the excited states of the dye in this solvent.

Discussion

The results show that the value of β for 2-methyl-2-pentene varies by at most a factor of four in the various solvents, since it would be an exceptional coincidence if both k_1 and k_2 were to vary by a large but exactly parallel amount in various solvents, and excited state lifetimes do not appear to vary much with solvent in any case (except when the solvent contains heavy atoms or when a charge-transfer interaction is possible). For example, Porter and Windsor observed only a small solvent effect on the lifetimes of triplet anthracene or naphthalene.[12] For these reasons, the variation in k_1 is not likely to be large, and thus the variation in k_2 is also probably not large. Because experimental error makes up a large proportion of the observed variation in β (although the differences between the extreme values are real), any rationalization of the variations is hazardous. However, the *lack* of correlation between the results and certain solvent properties is significant.

The most obvious property of solvent which might influence the rate would be the dielectric constant (or one of the other empirical measures of solvent polarity).[13] That no such correlation exists is immediately evident from Table I; for instance, the values of β in DMSO, acetone, CS_2, and benzene (D = 48.9, 20.7, 2.64, and 2.27) are all the same, within experimental error.

The rates of several "electroneutral" reactions (in which all participating species are neither ionic nor

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(10) C. S. Foote, S. Wexler, W. Ando, and R. Higgins, *J. Amer. Chem. Soc.*, **90**, 975 (1969).

(11) C. S. Foote, *Accounts Chem. Res.*, **1**, 104 (1968).

(12) G. Porter and M. W. Windsor, *Proc. Roy. Soc., Ser. A*, **245**, 238 (1958); *Discuss. Faraday Soc.*, **17**, 178 (1954).

(13) See E. M. Kosower, "An Introduction to Physical Organic Chemistry," Wiley, New York, N. Y., 1968, for a discussion of various solvent polarity parameters.

highly polar) have been correlated with the cohesive energy density of the solvent (its "internal pressure").[14] However, pyridine, DMF, and methanol, which fall at the high end of the internal pressure scale, have β values which bracket those for benzene and acetone, which fall at the low end, so that no correlation with this parameter is discernible.

Livingston and Owens reported that chlorophyll-sensitized photooxygenation of allylthiourea (ATU) showed a marked dependence on solvent viscosity, with the value of β being 0.1 *M* in methanol (η = 0.59 cP), but $\leq$0.001 *M* in cyclohexanol (η = 57 cP).[9] If the reaction of singlet oxygen with an acceptor is diffusion controlled, an increase in solvent viscosity should cause a marked *decrease* in reaction rate (k_2), which should be inversely proportional to the viscosity.[12] Although some decrease of the decay rate (k_1) might also be expected (Porter and Windsor found an effect proportional to the $^1/_2$ and $^1/_5$th power of viscosity on the lifetimes of triplet anthracene and naphthalene, respectively[12]), the net effect should be an *increase* in β (k_1/k_2) with viscosity, the opposite of the reported effect. However, since the rate of quenching of singlet oxygen by β-carotene is 2×10^4 times larger than the rate of its reaction with 2-methyl-2-pentene,[15] it is obvious that the rate of reaction is far less than diffusion controlled with this olefin, and thus also with ATU which has a comparable β value in methanol.[9] Thus the only effect of viscosity to be expected would be a possible small decrease in the decay rate and thus in the β value; comparison of the β values for 2-methyl-2-pentene in CH_3OH (0.16 *M*) and cyclohexanol (0.07 *M*) shows that the effect in this case is indeed small, and may not exceed the experimental error. The reported effects on the chlorophyll-sensitized oxidation of ATU are in apparent contradiction to these results. However, several features of the Livingston-Owens paper are puzzling; they also report a kinetic term which would require a diffusion-controlled quenching of singlet oxygen by chlorophyll, but neither chlorophyl *a* nor *b* appears to quench singlet oxygen appreciably.[16] Furthermore, there was evidence that at least two oxidation mechanisms were competing in the chlorophyll-sensitized oxidation of ATU, since there was a temperature-dependent and a temperature-independent component.[9] More recent studies of sensitized oxidations of ATU have shown that several mechanisms are operative, and it is not certain that a singlet oxygen mechanism is one of them, although it seems likely.[17]

Several reports of dramatic solvent effects on self-sensitized oxygenations of various anthracene derivatives have appeared; several were carried out with kinetic analysis which would separate sensitizer and β-value effects.[8] The most remarkable effect is a decrease in β by a factor of 12–60 in going from aromatic hydrocarbon solvents to CS_2.[8] No such effect was observed in this study, values of β in benzene and CS_2 being virtually identical (0.10 and 0.08 *M*), respectively.[17a] The reason for the reported effects in the anthracene cases is not certain; CS_2 strongly quenches the fluorescence of anthracene,[2,8] and these reactions will bear reinvestigation.[18]

Heavy atom solvents often markedly increase the rate of spin interconversion by spin-orbit coupling; for example, the rate of intersystem crossing in naphthalene increases by a factor of 50 on going from EPA to propyl iodide (glass, 77°K).[19] However, Eisenthal and El-Sayed found that charge-transfer complex formation with heavy atom containing acceptors did not measurably affect the *non*radiative transition probability, although a large effect on the radiative probability of triplet naphthalene and phenanthrene was found.[20] Any heavy-atom effect on the lifetime of singlet oxygen would be expected to increase β by increasing k_1. However, neither bromobenzene (β = 0.05 *M*) nor ethyl iodide (β = 0.11 *M*) shows such an effect when compared with benzene (β = 0.10 *M*).

The effect of dimethoxybenzene is interesting. No significant quenching of singlet oxygen is observed (β = 0.15 *M*); however, the tenfold increase in intercept in this solvent is an indication of strong quenching of *sensitizer* excited states, probably *via* a charge-transfer mechanism.[21] Evidently singlet oxygen is not quenched efficiently by this mechanism, although this solvent was chosen to test for this effect. Quenching of sensitizer but not singlet oxygen has also been observed with dimethylaniline in benzene and with *p-N,N*-dimethylaminotrimethylstyrene.[16a,22]

The observed range of solvent effects of less than a factor of four is comparable to that reported by Huisgen and Pohl for the "ene reaction" between 1,3-diphenylpropene and diethyl azodicarboxylate, which was interpreted by them as evidence against a dipolar mechanism.[23] The observed effects certainly argue against any large charge separation or highly polar species in the transition state for photooxygenation of 2-methyl-2-pentene. The lack of solvent effects coupled with the lack of directing effects of substituents[1] (which argues against *localized* charge or radical character) are most simply explained by a concerted mechanism. The six-center transition state **3** similar to that advanced for the ene reaction[23,24] and previously suggested for the photooxygenation on the basis of steric and conforma-

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[14] A. P. Stefani, *J. Amer. Chem. Soc.*, **90**, 1694 (1968).

[15] C. S. Foote and R. W. Denny, *ibid.*, **90**, 6233 (1968).

[16] (a) C. S. Foote and R. W. Denny, unpublished results. (b) The upper limit for any quenching was at least 40 times lower than the rate of β-carotene quenching. However, some self-quenching of chlorophyll *a* triplet was found, and both chlorophyll *a* and *b* react slowly with singlet oxygen.

[17] C. S. Foote, *Science*, **162**, 963 (1968); M. Nemoto, Y. Usui, and M. Koizumi, *Bull. Chem. Soc. Jap.*, **40**, 1035 (1967); H. E. A. Kramer and A. Maute, *Ber. Bunsenges. Phys. Chem.*, **72**, 1092 (1968).

[17a] NOTE ADDED IN PROOF. Recent redeterminations have given a value of β in CS_2 of 0.02 *M* (average of seven independent determinations). A study of the diffusion-controlled quenching by β-carotene suggests that the lifetime of $^1O_2$ is prolonged by a factor of 10 in CS_2.

[18] The dinaphthalenethiophene-sensitized photooxygenation of anthracene shows an effect of CS_2 on β identical with that reported for the self-sensitized reaction: E. Peterson and C. S. Foote, unpublished results.

[19] S. P. McGlynn, M. J. Reynolds, G. W. Daigre, and N. D. Crystodoyleas, *J. Phys. Chem.*, **66**, 2499 (1962).

[20] K. B. Eisenthal and M. A. El-Sayed, *J. Chem. Phys.*, **66**, 2499 (1962).

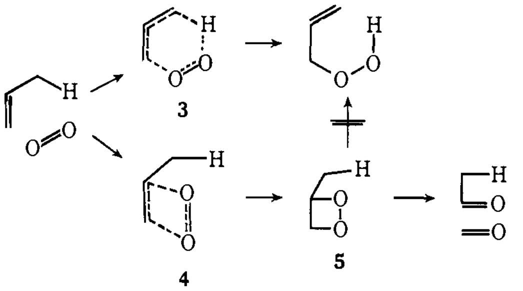
[21] H. Leonhardt and A. Weller, *Z. Phys. Chem.*, (*Frankfurt am Main*), **29**, 277 (1961); H. Leonhardt and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **67**, 791 (1963).

[22] However, DABCO and certain tertiary amines do quench singlet oxygen with moderate efficiency, in all probability by this mechanism: C. Oannés and T. Wilson, *J. Amer. Chem. Soc.*, **90**, 6528 (1968); C. S. Foote, R. W. Denny, L. Weaver, Y. Chang, and J. Peters, *Ann. N. Y. Acad. Sci.*, **171**, 139 (1970).

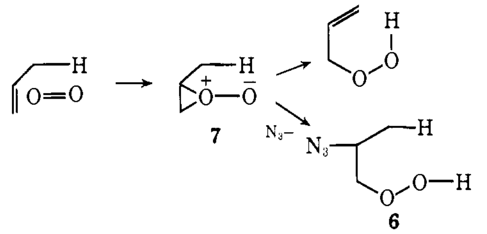
[23] R. Huisgen and H. Pohl, *Chem. Ber.*, **93**, 527 (1960).

[24] J. A. Berson, R. G. Wall, and H. O. Perlmutter, *J. Amer. Chem. Soc.*, **88**, 187 (1966); R. T. Arnold and J. F. Dowdall, *ibid.*, **70**, 2590 (1948); R. K. Hill and M. Rabinowitz, *ibid.*, **86**, 965 (1964).

tional considerations,[2,11,25] is entirely consistent with the results reported here and in the accompanying paper. However, a concerted 1,2 cycloaddition (four-center transition state **4**) recently advanced by Fenical, Radlick, and Kearns as an alternative to the ene reaction[26] is also consistent with the solvent and electronic effects reported here. However, a substituent effect on the direction of opening of dioxetane **5** might have been expected; this would have produced a variation in the product ratio for the trimethylstyrenes which was not observed.[1] Furthermore, several dioxetanes have now been prepared, and have been found to cleave to give carbonyl products.[27] In particular, that from 2-methyl-2-butene cleaves, and does not give the ene products,[27a] so that the dioxetane mechanism appears to be ruled out.



A variation on the dioxetane mechanism, originally put forward by Sharp[28] and, more recently, by Kopecky and Reich,[5] has recently received experimental support from the Kearns group.[29] Photooxygenations carried out in the presence of sodium azide produced azidohydroperoxides (**6**) instead of the normal ene product. It was suggested that **6** was produced by opening an intermediate perepoxide (**7**), which, if not trapped, rearranged to the normal ene product.



While this mechanism cannot be ruled out, the following facts argue against it. (1) Polar solvents would have been expected to increase the rate of formation of the zwitterion **7** at least modestly, although this cannot be stated with certainty. (2) Substituents should have had a marked effect on the direction of opening of **7** to ene product, with electron donors facilitating cleavage of the C–O bond to which they were attached. (3) The azide trapping experiments appear to be more complex than originally believed. While our investigation of the azide reaction is not complete, there is a very large decrease in the overall reaction rate, apparently caused by $^1O_2$ quenching.[30] At a minimum, this result requires that the role of azide is more than simply a trap for perepoxide **7**; it is not ruled out that azidohydroperoxides are formed by a different mechanism entirely.

In conclusion, the results reported here and in the accompanying paper are most easily accommodated by the cyclic transition state **3**; this transition state is also consistent with the known stereochemical requirements[25] of the reaction, but other mechanisms cannot be rigorously excluded. The reaction behaves in all respects like the ene reaction.[23,24]

Experimental Section

General conditions are as in ref 1. Peak areas were measured by planimeter. The data were fit by a least-squares program method for estimation of a rectangular hyperbola[31] translated into PL-1 language by Mr. Phil Bernard.

β-Value of 2-Methyl-2-pentene in Cyclohexanol. A solution containing 1.4413 g (0.017 mol) of 2-methyl-2-pentene, 7 mg (7×10^{-6} mol) of Rose Bengal, and 99 ml of cyclohexanol was poured into the photolysis apparatus previously described and regulated at a temperature of 25°.[1] After flushing with oxygen, the solution was photolyzed for exactly 6 min with a 625-W Sylvania Sungun incandescent lamp set at 50 V and regulated by a Sola constant voltage transformer.

After irradiation, 1.2 ml of trimethyl phosphite was added quickly and the solution was stirred for 5 min in the dark, then left overnight in a dark refrigerator; 0.0512 g (5.8×10^{-4} mol) of isoamyl alcohol was added as internal standard, and the thawed solution was again stirred for 20 min in the dark. The solution was then injected at 105° onto a 6 ft × $^1/_8$ in. column containing 15% Ucon-2000 polar on 80–100 Chromosorb W. From an average of three chromatograms, a mole ratio of 1:2.19 was determined for 2-methyl-3-penten-2-ol and isoamyl alcohol. After multiplication by a factor of 1.96 to include the 2-methyl-1-penten-3-ol isomer, a value of 45.8×10^{-5} mol of product was obtained from 1.717×10^{-2} mol of starting material, indicating a total conversion of 2.67%.

The above procedure was repeated for 1.1002, 0.7787, 0.5850, and 0.3553 g of 2-methyl-2-pentene and 43.6×10^{-5} (3.33%), 37.4×10^{-5} (4.03%), 33.3×10^{-5} (4.78%), and 23.6×10^{-5} mol (5.58%) of product were obtained. A least-squares fit of the data[31] indicated a slope of 11.1 (±0.5), a correlation coefficient of 0.995, and an intercept of 148 M^{-1} (±7.1), which gave a β value of 0.07 M with a standard deviation of ±0.01 M. Runs in other solvents were carried out in a similar manner.

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(25) A. Nickon and W. L. Mendelson, *J. Amer. Chem. Soc.*, **87**, 3921 (1965), and earlier papers; G. O. Schenck, K. Gollnick, G. Buchwald, S. Schroeter, and G. Ohloff, *Justus Liebigs Ann. Chem.*, **674**, 93 (1964).

(26) W. Fenical, D. R. Kearns, and P. Radlick, *J. Amer. Chem. Soc.*, **91**, 3396 (1969); D. R. Kearns, *ibid.*, **91**, 6554 (1969).

(27) (a) K. R. Kopecky and C. Mumford, *Can. J. Chem.*, **47**, 709 (1969); (b) P. D. Bartlett and A. P. Schaap, *J. Amer. Chem. Soc.*, **92**, 3223 (1970); (c) S. Mazur and C. S. Foote, *ibid.*, **92**, 3225 (1970).

(28) D. B. Sharp, Abstracts, 139th National Meeting of the American Chemical Society, New York, N. Y., Sept 1960, p 79p.

(29) W. Fenical, D. R. Kearns, and P. Radlick, *J. Amer. Chem. Soc.*, **91**, 7771 (1969).

(30) C. S. Foote and Y. C. Chang, unpublished results.

(31) K. R. Hanson, E. A. Havir, and R. Ling, *Biochem. Biophys. Res. Commun.*, **29**, 194 (1967).