3-21G basis set[19a] (denoted as 3-21G//3-21G), and single-point calculations were then carried out at the 3-21G optimized geometries with the polarized 6-31G* basis set[19b] (i.e., 6-31G*//3-21G). The calculations show that an α-silyl substituent is considerably less effective in stabilizing CH_3^+ than an α-methyl. At 6-31G*, $CH_3CH_2^+$ is more stable than $H_3SiCH_2^+$ by 13.2 kcal·mol^{-1} (eq 1).[5,20] An α-H_3Si substituent is, however, more stabilizing than hydrogen by 16.1 kcal·mol^{-1} (6-31G*//3-21G). β-Methyl substitution stabilizes $H_3SiCH_2^+$ somewhat more effectively than it stabilizes $CH_3CH_2^+$ so that $(CH_3)_3SiCH_2^+$ is less stable than $(CH_3)_3CCH_2^+$ by 11.0 kcal·mol^{-1} (eq 2, 3-21G//3-21G).[21,22] These results are surprising in light of the lower electronegativity of silicon compared to carbon (Pauling's electronegativities: Si, 1.8; C, 2.5[23a]) and the fact that $(CH_3)_3Si$ is a stronger σ donor than t-Bu (σ_I values are −0.11 and −0.01, respectively[23b]). The calculations show that the destabilizing effect of silyl groups (relative to alkyl groups) results from a weaker hyperconjugation and from the electrostatic repulsion between the adjacent positively charged cationic carbon and silicon. Note, however, that α-alkyl and α-silyl substituents stabilize vinyl cations to a similar extent.[24]

$$\mathrm{H_3SiCH_2^+ + CH_3CH_3 \rightarrow H_3SiCH_3 + CH_3CH_2^+} \qquad (1)$$

$$\mathrm{(CH_3)_3SiCH_2^+ + (CH_3)_4C \rightarrow (CH_3)_4Si + (CH_3)_3CCH_2^+} \qquad (2)$$

The energy differences between the ground states of **1** and **2** (modeled computationally by the corresponding alcohols[25]) are relatively small (eq 3a and 3b[26]). Equation 4b, which models the S_N1 reactivities of **1** and **2** more closely than eq 2,[25,26] is therefore also highly exothermic.

$$\mathrm{R_3SiCH_2OH + R_3CCH_3 \rightarrow R_3SiCH_3 + R_3CCH_2OH}$$

$$\mathrm{R = H} \quad \Delta E = -7.6\ \mathrm{kcal{\cdot}mol^{-1}} \quad \text{6-31G*//3-21G} \qquad (3a)$$

$$\mathrm{R = CH_3} \quad \Delta E = -5.9\ \mathrm{kcal{\cdot}mol^{-1}} \quad \text{3-21G//3-21G} \qquad (3b)^{22}$$

$$\mathrm{R_3SiCH_2^+ + R_3CCH_2OH \rightarrow R_3SiCH_2OH + R_3CCH_2^+}$$

$$\mathrm{R = H} \quad \Delta E = -5.6\ \mathrm{kcal{\cdot}mol^{-1}} \quad \text{6-31G*//3-21G} \qquad (4a)$$

$$\mathrm{R = CH_3} \quad \Delta E = -3.8\ \mathrm{kcal{\cdot}mol^{-1}} \quad \text{3-21G//3-21G} \qquad (4b)^{22}$$

We conclude that the S_N1 reactivity of neopentyl derivatives (**2**) is considerably higher than that of the corresponding silyl derivatives (**1**).

The effect of silyl substitution at carbon on the S_N2 reactivity is even more dramatic. The calculated barriers for the S_N2 hydride exchange reactions[27] 5a, 5b, and 5c are 47.4 (44.3), 50.1 (47.4), and 35.9 (35.3) kcal·mol^{-1}, respectively, at 6-31G*//3-21G (the values in parentheses are at 3-21G//3-21G).

$$\mathrm{H^- + CH_3R \rightarrow [H{\cdots}CH_2R{\cdots}H]^- \rightarrow H^- + CH_3R}$$

$$\mathrm{R = H\ (5a) \qquad R = CH_3\ (5b) \qquad R = H_3Si\ (5c)}$$

$$\mathrm{R = (CH_3)_3C\ (5d) \qquad R = (CH_3)_3Si\ (5e)}$$

The dramatic lowering of the S_N2 barrier by R = H_3Si results primarily from the fact that H_3Si is a better σ acceptor than CH_3[28] and therefore stabilizes the negatively charged transition state more effectively. The barrier in the S_N2 reaction for C_2H_6 is only 2.7 kcal·mol^{-1} higher than for CH_4, but for neopentane steric crowding in the transition state raises the barrier significantly to 52.0 kcal·mol^{-1} (eq 5d, 3-21G//3-21G). Due to the long C–Si bonds, steric crowding in the transition state for eq 5e is much smaller than in the carbon analogue for eq 5d and the barrier for substitution at $(CH_3)_3SiCH_3$ is 33.0 kcal·mol^{-1} (eq 5e, 3-21G//3-21G),[29] *20 kcal·mol^{-1} lower* than for $(CH_3)_3CCH_3$.[30]

In conclusion, both calculations and experimental data indicate that *silylcarbinyl sulfonates, **1**, react slower than their neopentyl analogues, **2**, via the S_N1 mechanism, but faster than **2** via the S_N2 mechanism.*

Acknowledgment. We are grateful to the donors of Petroleum Research Fund, administered by the American Chemical Society, and the NSF (CHE 81-07629) for partial support of this work, as well as the NSF's two- and four-year College Research Equipment Program for assistance in the purchase of rate data acquisition equipment. We thank Professors J. A. Pople and M. S. Gordon for providing us with the 3-21G and the 6-31G* basis sets for silicon prior to publication, Dr. S. Topiol for an IBM version of GAUSSIAN 80, the U.S.–Israel BSF, Jerusalem, for partial support, and the Technion's Computer Center for a generous donation of computer time. We also thank Bruce Taggart for assistance with some initial experiments.

Registry No. **1a**, 59006-07-4; **1b**, 64035-64-9; **5a**, 74-82-8; **5b**, 74-84-0; **5c**, 992-94-9.

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(19) (a) First row: Binkley; J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939–947. Second row: Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *Ibid.* **1982**, *104*, 2797–2803. (b) First row: Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213–222. Second row: Pietro, W. J.; Francl, M. M.; Hehre, W. J.; DeFrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am Chem. Soc.* **1982**, *104*, 5039–5048.

(20) (a) This result is in excellent agreement with the computations of the following: Hopkinson, A. C.; Lien, M. H. *J. Org. Chem.* **1981**, *46*, 998–1003. (b) The minimal STO-3G basis set leads to erroneous results (see: Apeloig, Y.; Schleyer, P. v. R.; Pople, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 1291–1296, and ref 23), and it should be applied to molecules that contain silicon with great caution.

(21) This applies to the classical structures. At 3-21G $(CH_3)_3SiCH_2^+$ does not collapse to $(CH_3)_2Si^+CH_2CH_3$.[15]

(22) Our experience shows that the calculated energies of such isodesmic equations are practically identical at 6-31G*//3-21G and 3-21G//3-21G.

(23) (a) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 93. (b) Charton, M. *Prog. Phys. Org. Chem.* **1981**, *13*, 119–251.

(24) (a) Apeloig, Y.; Stanger, A. *J. Org. Chem.* **1982**, *47*, 1462–1468. (b) Schiavelli, M. D.; Jung, D. M.; Vaden, A. K.; Stang, P. J.; Fisk, T. E.; Morrison, D. S. *Ibid.* **1981**, *46*, 92–95.

(25) The validity of this approach is discussed in ref 24a.

(26) ΔE of eq 3b for the sulfonates is probably even less exothermic due to F strain between the sulfonate and the $(CH_3)_3C$ substituent.

(27) Given by the energy difference between the reactants and the transition state which was assumed to possess C_s (D_{3h} in CH_5^-) symmetry. The symmetry plane is defined by the central carbon and the two apical hydrogens.

(28) The calculated proton affinity of $H_3SiCH_2^-$ is 33.0 kcal·mol^{-1} lower than that of $CH_3CH_2^-$.[20a]

(29) Thus, methyl substitution reduces the S_N2 barrier by 2.3 kcal·mol^{-1}, probably due to the better charge dispersal in the negatively charged transition state by the larger $(CH_3)_3Si$ substituent.

(30) Similar results are obtained for the analogous fluoride-exchange reactions.

Ene Reaction of Singlet Oxygen: An Entropy-Controlled Process Determines the Reaction Rate

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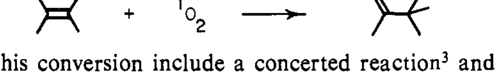
Received August 18, 1982

The chemistry of singlet oxygen ($^1\Delta_g$, $^1O_2$) has been extensively studied and is of continuing interest.[1] The "ene" reaction of $^1O_2$ with olefins containing an allylic hydrogen is a synthetically useful route to allylic hydroperoxides[2] (eq 1). Proposed mechanisms for this conversion include a concerted reaction[3] and stepwise sequences proceeding through a biradical (**1**, Chart I),[4] a zwitterion



(1)

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(1) (a) Wasserman, H. H., Murray, R. W., Eds. "Singlet Oxygen"; Academic Press: New York, 1979. (b) Ranby, B., Rabek, J. F., Eds. "Singlet Oxygen Reactions with Organic Compounds and Polymers"; Wiley: New York, 1978.

(2) Schenck, G. O.; Ziegler, K. *Naturwissenschaften* **1944**, *32*, 157. Denny, R. W.; Nickon, A. *Org. React.* **1973**, *20*, 133.

(3) Gollnick, K.; Kuhn, H. J., in ref 1a, p 341.

(4) Harding, L. B.; Goddard, W. A., III *J. Am. Chem. Soc.* **1977**, *99*, 4520; **1980**, *102*, 439.

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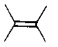
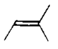
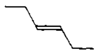
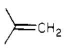
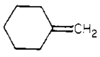
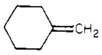
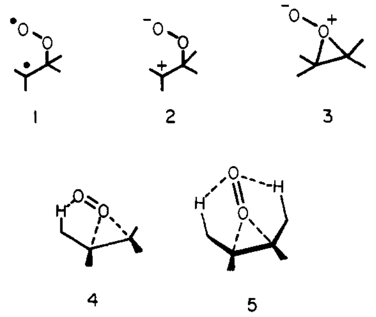
Table I. Reaction of $^1O_2$ with Various Olefins

olefin	solvent	IP,[a] eV	$\Delta H^\ddagger$,[b] kcal/mol	$\Delta S^\ddagger$,[b] eu	$\Delta S^\ddagger_{norm}$, eu	k_q,[c] $M^{-1}\ s^{-1}$	k_r,[d] $M^{-1}\ s^{-1}$
	CS_2	8.34	0.5	−23	−30	2.2×10^7	4.0×10^{-7}
	CS_2	8.82	0.7	−30	−31[e]	7.2×10^5	2.4×10^{-6}
	$(CD_3)_2CO$		1.1	−27	−28[e]	1.3×10^6	
	CS_2	9.13	1.6	−32	−35	4.8×10^4	
	CS_2		2.0	−31	−34	3.9×10^4	
	CS_2	9.12	1.2	−32	−35	5.8×10^4	8.7×10^{-4}
	CS_2	9.13	0.3	−42	−45	7.2×10^3	1.2×10^{-4}
	CS_2	9.16	0.4	−39	−42	7.7×10^3	
	CS_2	9.35	0	−43	−46	4.0×10^3	8.9×10^{-4}
	CS_2	9.14	−0.1	−42	−45	5.2×10^3	
	$(CD_3)_2CO$		−0.2	−42	−45	6.1×10^3	

[a] Taken from the compilation in ref 17. [b] The reproducibility of independent runs for $\Delta H^\ddagger$ is estimated to be ±0.8 kcal/mol and for $\Delta S^\ddagger$ 1.0 eu. [c] Calculated for 25 °C from the measured activation parameters. [d] These values are for methanol solution at 25 °C and depend on the value of the $^1O_2$ lifetime chosen. The rate constants are taken from the compilation in ref 17. [e] In the normalization of $\Delta S^\ddagger$ for this compound only two "equivalent" sites were assumed since reaction occurs primarily from the more "crowded" side[10] in essentially equal amounts.[3]

Chart I



(**2**)[5] or perhaps a perepoxide (**3**).[6,7] Recently Stephenson and co-workers have shown that the product-forming and rate-limiting steps are different in the reaction of $^1O_2$ with tetramethylethylene[8] and other olefins.[9] This finding is interpreted to indicate operation of a two-step mechanism. First an association of $^1O_2$ and the olefin occurs in which the cis-methyl groups are still chemically equivalent, then a second step differentiates between the methyl groups according to isotopic substitution. Also of special interest is the observation that trisubstituted olefins react with $^1O_2$ predominantly on the more crowded side.[10] These results, among others, moved Stephenson to incorporate a species (**4**, **5**), similar to one posited by Bartlett and co-workers,[7] involving early bonding to the allylic hydrogens in the ene reaction sequence. Herein we report the results of a kinetic investigation of the mechanism of the ene reaction. We find an essentially solvent-independent 10 000-fold variation in reaction rate for different olefins that is determined almost entirely by the changes in the activation entropy. Moreover, the olefins we have investigated appear to fall naturally into two distinguishable groups: those that have two allylic hydrogen-bearing alkyl groups with a cis relationship ("cis" olefins), and those that do not have this substitution pattern ("non-cis" olefins). These findings indicate that the transition state for the ene reaction depends on the substitution pattern of the olefin. This simple structural criterion appears to predict reliably the relative reactivities of simple alkenes and the site of reaction for more complex polyenes.[11]

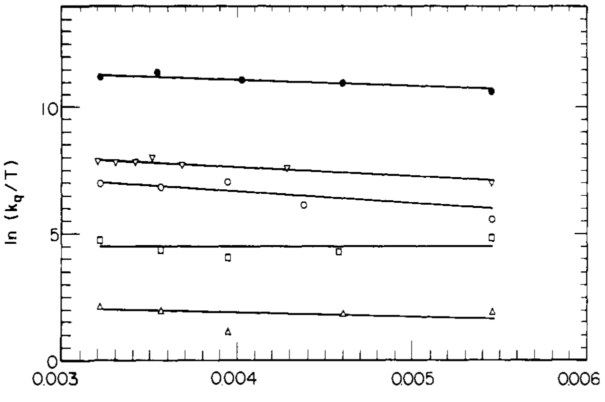


Figure 1. Erying plots of quenching rate constants for several olefins: (△) *trans*-2-butene; (□) isobutylene; (○) *cis*-2-butene; (▽) trimethylethylene; (●) tetramethylethylene.

Recently we reported measurement of the lifetime of $^1O_2$ in solution.[12] We have used this technique to measure the rate constants for reaction of a series of olefins with $^1O_2$ generated by tetraphenylporphyrin sensitization in carbon disulfide or perdeuterated acetone solution over the temperature range −90 to 37 °C. The pseudo-first-order lifetime of $^1O_2$ in CS_2 (3.4 ms)

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(5) Jefford, C. W. *Tetrahedron Lett.* **1979**, 985. Jefford, C. W.; Rimbault, C. G. *J. Am. Chem. Soc.* **1978**, *100*, 295.

(6) Sharp, D. B. "Abstracts of Papers", 138th National Meeting of the American Chemical Society; American Chemical Society; Washington, DC, 1960; p 70.

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(8) (a) Stephenson, L. M.; Grdina, M. J.; Orfanopoulos, M. *Acc. Chem. Res.* **1980**, *13*, 419. (b) Stephenson, L. M. *Tetrahedron Lett.* **1980**, *21*, 1005.

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(10) (a) Orfanopoulos, M. G.; Grdina, M. B.; Stephenson, L. M. *J. Am. Chem. Soc.* **1979**, *101*, 275. (b) Lerdal, D.; Foote, C. S. *Tetrahedron Lett.* **1978**, 3227. (c) Schulte-Elte, K. H.; Muller, B. L.; Pamingle, H. *Helv. Chim. Acta* **1979**, *62*, 816.

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is shortened as the olefin concentration is increased. Analysis of these data provides the bimolecular rate constants (k_q) for these reactions. Figure 1 shows the temperature dependence of these rate constants for a representative group of olefins plotted according to the Eyring formalism. The activation parameters obtained from this treatment are presented in Table I.

It is immediately apparent from inspection of Table I that the variation of k_q for all olefins examined appears primarily to be a response to change in $\Delta S^{\ddagger}$ rather than $\Delta H^{\ddagger}$. A similar result has been reported previously for the reaction of $^1O_2$ in toluene with furans and indoles.[13] In the present case nonzero $\Delta H^{\ddagger}$ are obtained, but in most instances they do not differ significantly from zero or from each other. The apparent lack of correlation between change in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for different olefins is reasonably a manifestation of multiple interaction mechanisms.[14]

Interpretation of the effect of olefin structure on $\Delta S^{\ddagger}$ requires normalization for the destruction of external rotational symmetry, when it exists, in the starting olefin.[15] For example, tetramethylethylene has three 2-fold rotation axes, which are not likely to be preserved at the transition state. In comparison, trimethylethylene does not lose any such symmetry when it reacts. Similarly $\Delta S^{\ddagger}$ must be adjusted statistically for the number of apparently equivalent reactive sites;[16] four for tetramethylethylene, two for *cis*-2-butene, etc. These normalized activation entropies ($\Delta S^{\ddagger}_{norm}$) are listed in Table I.

The results presented in Table I reveal considerable information about the mechanism of the ene reaction. The most reactive olefin has k_q ca. 3 orders of magnitude below the diffusion limit. Thus there are many nonproductive collisions for every one that leads to consumption of $^1O_2$. These collisions may lead to a weakly bound exciplex or may simply be nonbinding encounters. Comparison of k_q with previously reported values for the consumption of oxygen by these olefins in methanol[17] (k_r) and the observation that quantum yields for reaction approach unity at high olefin concentration indicate that k_q is primarily a measure of the reaction rate and not of physical quenching of $^1O_2$.

The $\Delta S^{\ddagger}_{norm}$ values appear to fall clearly into two groups, the cis olefins and the non-cis olefins, indicating a change in transition-state structure between these classes. The magnitude of $\Delta S^{\ddagger}$ does not depend on the solvent, and, therefore, probably reveals intrinsic properties of the transition state. Gas-phase dimerization of cyclopentadiene, a prototypical bimolecular reaction with an ordered transition state, has $\Delta S^{\ddagger} = -34$ eu.[18] Comparison with our $\Delta S^{\ddagger}_{norm}$ shows that the transition state for the cis olefins is somewhat less constrained than that of the prototype and that for their non-cis counterparts is more constrained.[19]

These findings support the path for the ene reaction described by Stephenson[8a] and by Bartlett.[7] Thus, the initial reversibly formed encounter complex, or exciplex, of $^1O_2$ and olefin is not in the required reaction geometry. Movement to this geometry is the irreversible entropy-controlled process that brings the reactants to the transition state. The systematic grouping of $\Delta S^{\ddagger}_{norm}$ indicates that this transition state already reflects the preference for reaction on the more crowded side and the interaction of the allylic hydrogen with an oxygen atom that is required of the postulated reaction "intermediate". Structure **4** for non-cis olefins and structure **5** for cis olefins with the oxygen loosely directed toward the allylic hydrogens[19] are representations of the transition state consistent with all available data.

Consistent with the theoretical analysis of Kearns,[21] Paquette and co-workers[11] noted that the relative reactivity of various sites on polyenes toward $^1O_2$ can be predicted by consideration of "isolated" ionization potentials. It is apparent from our data that the ionization potential is not the sole determinant of reaction rate. For example, *cis*- and *trans*-2-butene have identical ionization potentials, but they differ considerably in reactivity. However, within a class, the cis olefins for example, there is some correlation of ionization potential with reactivity, and this is reflected in the measured $\Delta H^{\ddagger}$. Thus, it appears that "donor-acceptor" interactions play some role in the transition state for the ene reaction. The simple observation that non-cis olefins react slower than cis olefins permits accurate prediction of the site of reactivity of alkenes[20] and polyenes. Consideration of the ionization potentials may permit further discrimination among olefins within a class.

Acknowledgment. We thank James Fenton for his help with the laser system, Charles Hawley for his assistance with the electronic devices, and Professor L. M. Stephenson of the University of Southern California for his many thoughtful suggestions. This research was supported in part by a grant from the National Science Foundation and in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. $^1O_2$, 7782-44-7; tetramethylethylene, 563-79-1; trimethylethylene, 513-35-9; *cis*-2-butene, 590-18-1; *cis*-2-pentene, 627-20-3; cyclopentene, 142-29-0; *trans*-2-butene, 624-64-6; *trans*-2-pentene, 646-04-8; 1,1-dimethylethylene, 115-11-7; methylenecyclohexane, 1192-37-6.

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(16) Reference 14, p 133. The number of equivalent sites is dependent on the actual mechanism of the reaction. We have chosen the most general case with each methyl group as apparently equivalent. However, the mechanism we suggest below indicates that two cis groups can be counted as one site. The conclusions are independent of the counting scheme.

(17) Reference 3, pp 291-295.

(18) Wasserman, A. *Montatsh. Chem.* **1982**, *83*, 542.

(19) Reference 14, pp 68-69.

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Amphoteric Ligands. 1. Facile Acyl Formation and Crystal Structure of a Novel Complex Containing an η^2(C,O)-Acylphosphonium Ligand[†]

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Irvine, California 92713

Received July 6, 1982

Reduction of carbon monoxide with hydrogen is difficult to achieve. Simultaneous activation at both C and O should substantially weaken the CO bond and facilitate reaction with metal-bound hydrogen.[1] A complex containing an amphoteric ligand—one that has both metal- and oxygen-binding centers—appears particularly attractive, as the chelate effect will contribute to other factors[2] tending to stabilize reduced forms of CO in such a molecule. In this and the following communication[3] we report that such ligands can indeed greatly facilitate formation of CO insertion products, although neither the structure of the product nor the mechanism of its formation need always correspond to straightforward expectations.

In choosing a suitable system, a key consideration will be minimizing self-aggregation of the amphoteric ligand. Ph_2PN-*t*-$BuAlEt_2$ is reported to be monomeric in solution (according to cryoscopy in benzene[4]) and should be a suitable choice. We have prepared a series of aluminoaminophosphines, $R_2PNR'AlR''_2$, **1**,

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[†] This and the following paper are dedicated to the memory of Martin B. Dines, friend and colleague, 1943-1982.

(1) See, for example: Rofer-DePoorter, C. K. *Chem. Rev.* **1981**, *81*, 447-474. Muetterties, E. L.; Stein, J. *Ibid.*, **1979**, *79*, 479-490. Herrmann, W. A. *Angew Chem., Int. Ed. Engl.* **1982**, *21*, 117-130.

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