

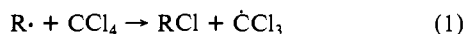
The Free Radical Reaction between Alkanes and Carbon Tetrachloride¹

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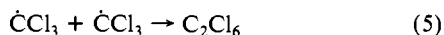
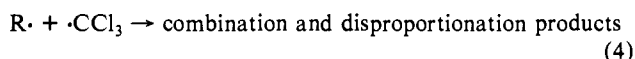
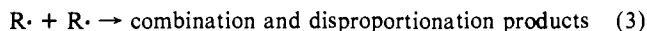
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Received November 13, 1984. Revised Manuscript Received April 2, 1985

Abstract: Product studies and kinetic electron paramagnetic resonance methods were used to investigate the free radical reaction between alkanes and carbon tetrachloride in solution. Trichloromethyl radicals abstracted hydrogen from simple alkanes with rate constants of ca. $60 \text{ M}^{-1} \text{ s}^{-1}$ at 300 K, in good agreement with gas-phase data. However, rate constants for chlorine abstraction by alkyl radicals from carbon tetrachloride were ca. $10^4 \text{ M}^{-1} \text{ s}^{-1}$ and were therefore ca. 2 orders of magnitude higher in solution than in the gas phase. Possibilities for the origin of this effect are discussed.

Alkanes react with carbon tetrachloride by a free radical chain mechanism. The propagation steps yield alkyl chloride and chloroform as molecular products (eq 1, 2). These reactions have



been studied extensively in the gas phase,⁵⁻¹⁰ and under carefully selected conditions products have also been detected from all of the termination reactions (eq 3-5). From these results, the ratios



$k^1/(2k_3)^{1/2}$ and $k_2/(2k_5)^{1/2}$ have been calculated, and since both k_3 and k_5 are known, the experiments yield the rate constants for the propagation steps.⁵⁻¹⁰

Reaction 2 appears to be influenced by thermodynamic factors. Thus, activation energies decrease as the C-H bond dissociation energy in the alkane decreases.⁹ However, the effect is offset to some extent by compensating decreases in the Arrhenius A factors.⁹ There appear to be no serious experimental difficulties with this reaction since studies from different laboratories are in reasonable accord.^{6-8,10}

Studies of reaction 1 suggest that the rate constants are essentially insensitive to the nature of the alkyl radical involved.⁹ However, taken as a whole, the literature data for the kinetics of these reactions are in disarray. Reports of their gas phase rate constants⁸⁻¹¹ are often orders of magnitude different from the limited amount of available solution data.¹²⁻¹⁵

Since reaction 1 has often been used to trap carbon-centered radicals,⁵⁻¹³ we felt that it would provide a useful kinetic standard for competition studies. We have therefore attempted to resolve the difficulties with the reaction kinetics by using a common experimental approach to measure k_1 for different alkyl radicals. In addition, we have measured rate constants for reaction 2 in solution.

Experimental Section

Materials. All hydrocarbons, carbon tetrachloride, and bromotrichloromethane were commercially available in high purity (GC analysis) and were therefore used as received. Di-*tert*-butyl peroxide (K and K) was washed with aqueous silver nitrate to remove olefinic impurities. It was then washed with water, dried over magnesium sulfate, and finally passed through a column of alumina. Hexamethylditin, trimethyltin chloride, and trimethyltin bromide were commercially available and were distilled before use.

Apparatus. Electron paramagnetic resonance (EPR) spectra were recorded on a Varian E104 spectrometer, and radicals were generated by direct photolysis of samples placed in the spectrometer cavity.

The photolysis source was a 1000-W mercury-xenon arc lamp, and its output was filtered through an aqueous solution of nickel and cobalt sulfates to remove much of the visible and most of the infrared radiation. The light was further filtered through a Pyrex plate (cut-off 316 nm) to prevent the direct photolysis of carbon tetrachloride.

Measurements of radical concentrations were taken immediately after the start of photolysis so as to avoid any problems associated with sample depletion. In some instances, a flow system was used as a check on this technique. This consisted of a cylindrical quartz tube (optical pathlength 4 mm) which was positioned in the cavity in an appropriately designed variable-temperature dewar. The flow rate was maintained at 0.2-2 mL min^{-1} by using a syringe drive. The flow system gave results that were, within the limits of experimental error, identical with those obtained with the static tubes.

Radical concentrations were measured by double integration of appropriate lines in the EPR spectra and were calibrated against standard solutions of diphenylpicrylhydrazyl in benzene. The signal from a ruby disk, placed in the spectrometer cavity, was used to correct for the differences in the sensitivity of the spectrometer towards the different solutions.

Product Analysis. Samples for product analyses were photolyzed in a home-built reactor fitted with a carousel so as to ensure uniform irradiation. Photolyses were carried out by using 350-nm lamps, but since these tend to emit a broad band of radiation, the light was further filtered through soda glass (15% transmission at 330 nm).

Products were analyzed on a Varian 3600 GC chromatography that was fitted with an OV-101 or capillary columns. *tert*-Butylbenzene was used as an external standard. GC/mass spectra were obtained with a Hewlett-Packard 5995 instrument equipped with a capillary column (HP 102-5-10C).

(1) Issued as NRCC publication No. 24555.
(2) National Research Council of Canada.
(3) Rice University.
(4) University of York.
(5) Tedder, J. M.; Watson, R. A. *Trans. Faraday Soc.* **1966**, *62*, 1215.
(6) White, M. L.; Kuntz, R. R. *Int. J. Chem. Kinet.* **1971**, *3*, 127.
(7) Wampler, F. B.; Kuntz, R. R. *Int. J. Chem. Kinet.* **1971**, *3*, 283.
(8) Currie, J.; Sidebottom, H.; Tedder, J. *Int. J. Chem. Kinet.* **1974**, *6*, 481.
(9) Matheson, I.; Tedder, J.; Sidebottom, H. *Int. J. Chem. Kinet.* **1982**, *14*, 1033.
(10) Matheson, I.; Tedder, J.; Sidebottom, H. *Int. J. Chem. Kinet.* **1983**, *15*, 905.
(11) Macken, K. V.; Sidebottom, H. W. *Int. J. Chem. Kinet.* **1979**, *11*, 511.
(12) Frith, P. G.; McLauchlan, K. A. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 87.
(13) Katz, M. G.; Horowitz, A.; Rajenbach, L. A. *Int. J. Chem. Kinet.* **1975**, *7*, 183.

(14) Paul, H. *Int. J. Chem. Kinet.* **1979**, *11*, 495.
(15) Lindsay, D. A.; Luszyk, J.; Ingold, K. U., submitted for publication in *J. Am. Chem. Soc.*

Table I. Products Obtained by Photolysis of Di-*tert*-butyl Peroxide in the Presence of Alkanes (RH) and Carbon Tetrachloride^a

RH	[RH], M	[<i>t</i> -BuOH], mM	[HCCl ₃], mM	[RCI], mM	[C ₂ Cl ₆], mM	[R ₂]
cyclopentane ^a	3.22	24	26	47	14	0
cyclohexane ^a	2.77	27	15	45	14	0
isobutane ^b	3.32	104 ^c	70 ^d	<i>e</i>		<i>e</i>
1,4-cyclohexadiene ^f	3.17	47	50	0	0	<i>g</i>
toluene	2.82	20	30	0	0	<i>g</i>

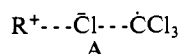
^a Rates of initiation were ca. 10^{-5} – 10^{-6} M⁻¹ s⁻¹ and were accurately quantified by dividing [*t*-BuOH] by the photolysis time (40 min). ^b Solution photolyzed in a sealed NMR tube for 120 min. ^c By GC analysis of a matched sample containing di-*tert*-butyl peroxide and cyclohexane, $R_{C_2Cl_6}$ (eq 10) was taken to be (R_{t-BuOH})/2. ^d By NMR. ^e Not detected by NMR. ^f Photolyzed for 80 min. ^g Present, but no quantified (see text).

All samples were deoxygenated by using at least three freeze–pump–thaw cycles or by nitrogen purging.

Results and Discussion

The most comprehensive gas-phase study of reactions 1 and 2 was carried out by Matheson, Tedder, and Sidebottom,⁹ who found values of k_2 which agreed with results obtained by other workers and which increased as the C–H bond dissociation energy in the alkane decreased. By contrast, values of k_1 showed little variations; thus, k_1 (M⁻¹ s⁻¹) = 1.0×10^4 (Me·), 2.0×10^4 (Et·), and 5.0×10^3 (*i*-Pr·) in the gas phase at 150 °C.¹⁶ The measured activation energies for these reactions⁹ suggest that the corresponding values of k_1 should fall into the range 10 – 10^2 M⁻¹ s⁻¹ at 25 °C. While this work probably represents the most authoritative study of the reaction in the gas phase, it should be noted that the data are in conflict with results for the reaction in solution.

Rate constants for the reaction of *tert*-butyl and cyclohexyl radicals with carbon tetrachloride in solution were found to be 4.9×10^4 M⁻¹ s⁻¹ at 37 °C¹² and 1.9×10^5 M⁻¹ s⁻¹ at 60 °C,¹³ respectively. While two very different and unusual techniques were used for the measurements, the differences between the solution and the gas-phase data are substantial. It has been proposed¹² that contributions from charge separation in the transition state for the reaction may account for the dramatic difference, since these may be assisted by solvation (A).



The situation creates a dilemma for any investigator using carbon tetrachloride in solution as a trap for alkyl radicals, since it is by no means clear that all of the data are reliable and that the differences between the gas-phase and the solution results are real.

In an attempt to resolve some of these difficulties, we decided to measure rate constants for both propagation steps in solution.

Product Studies. A series of experiments, based on product studies, was carried out to identify the propagation reaction (1 or 2) which was rate controlling in solution at 25 °C. In several instances rate constants for the rate-controlling step were obtained from these analytical data.

Product studies of the reaction were carried out by photolyzing ($\lambda > 325$ nm) mixtures of carbon tetrachloride (2.1 M), di-*tert*-butyl peroxide (4.1 M), and alkane (ca. 3 M) at 25 °C and to ca. 2% conversion. The products were identified by GC/mass spectrometry and were quantified by the use of authentic samples

(16) The value obtained for cyclohexyl⁸ ($k_1 = 3.2 \times 10^2$ M⁻¹ s⁻¹ at 150 °C) is likely to be in error since the data led to an unusually low value ($\leq 10^7$ M⁻¹ s⁻¹) for the self-reaction of cyclohexyl radicals. While the contemporary literature^{17,18} supported such a possibility, the notion that alkyl radicals would undergo self-reaction with significantly lower rate constants than those for diffusion control (10^9 – 10^{10} M⁻¹ s⁻¹) was later discounted.¹⁹

(17) McMillen, D. F.; Golden, D. M.; Benson, S. W. *J. Am. Chem. Soc.* **1972**, *94*, 4403.

(18) Hiatt, R.; Benson, S. W. *Int. J. Chem. Kinet.* **1973**, *5*, 375.

(19) Griller, D.; Ingold, K. U. *Int. J. Chem. Kinet.* **1974**, *6*, 453.

(20) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317.

Table II. Solution and Gas-Phase Rate Constants for the Reactions of Trichloromethyl Radicals with Several Alkanes at 300 K

RH	k_2 (solution) ^a , M ⁻¹ s ⁻¹	k_2 (gas phase), M ⁻¹ s ⁻¹
cyclopentane	74	14 ^{b,c}
cyclohexane	49	10 ^d
isobutane	54	132 ^e

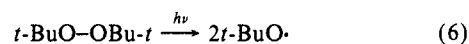
^a This work. ^b Reference 10. ^c Reference 7. ^d Reference 6. ^e Reference 9.

Table III. Heats of Reactions 1 and 2 for a Variety of Alkanes as Substrates^a

	$\Delta H(1)$, kcal mol ⁻¹	$\Delta H(2)$, kcal mol ⁻¹
cyclopentane	-8.8	-0.3
cyclohexane	-8.8	-0.3
isobutane ^b	-8.9	-1.6
toluene	-1.1	-7.8
1,4-cyclohexadiene	14.9 ^c	-21.8 ^d

^a Data taken from: Cox, J. D.; Pilcher, G.; "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1970. McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493. ^b ΔH_f (*t*-Bu·) taken from: Castelhan, A. L.; Griller, D. *J. Am. Chem. Soc.* **1982**, *104*, 3655. ^c ΔH_f (1-chloro-2,5-cyclohexadiene) = 18.5 kcal mol⁻¹, estimated from group additivity contributions (ref 23). ^d C–H bond dissociation energy in 1,4-cyclohexadiene = 74 ± 2 kcal mol⁻¹; Griller, D.; Burkey, T. J.; unpublished results.

as standards. The reactions are described in eq 1–6, and the product yields are given in Table I.



When the alkanes were cyclopentane or cyclohexane, the only product of the termination reactions 3–5 was hexachloroethane. This observation indicates that abstraction of hydrogen from the alkane by $\overset{\cdot}{C}Cl_3$ (eq 2) was the rate-determining step for the chain reaction. The relatively large amount of hexachloroethane shows that chain lengths were short, ca. 3, and that, within experimental error, the reactions conformed to the following material balances dictated by reactions 1–5.

$$[t\text{-BuOH}] = 2[C_2Cl_6] \quad (8)$$

$$[RCI] = [HCCl_3] + 2[C_2Cl_6] \quad (9)$$

Application of the steady-state approximation to these reactions led to eq 10, in which R_{HCCl_3} and $R_{C_2Cl_6}$ represent the rates of formation of chloroform and hexachloroethane.

$$R_{HCCl_3}/(R_{C_2Cl_6}^{1/2}[RH]) = k_2/k_5^{1/2} \quad (10)$$

Substitution in that equation of the data obtained by product analyses gave values of $k_2/(k_5)^{1/2}$. Using the literature value¹⁴ of $k_5 = 2.9 \times 10^9$ M⁻¹ s⁻¹, we obtained the values k_2 reported in Table II.

The rate constants measured in solution were in excellent agreement with the related gas-phase values, bearing in mind that the Arrhenius parameters for the gas-phase data were based on experiments carried out at ca. 150 °C (Table II). We attach no special significance to the small variations of k_2 for the solution data since the experimental errors are ca. $\pm 20\%$. However, in broad terms k_2 was fairly insensitive to the structures of these simple hydrocarbons.

For RH = 1,4-cyclohexadiene or toluene, dimers of the alkyl radicals derived were found to be the termination products and hexachloroethane was not detected. Thus, for these substrates, the chain could no longer be propagated through reaction 1. Nevertheless, it was possible to test the efficiency of reaction 2 by first generating trichloromethyl radicals by an alternate route.

The method chosen involved photolysis (350 nm) of mixtures typically containing hexamethylditin (0.2 v/v) bromotrichloromethane (0.5 v/v) and 1,4-cyclohexadiene or toluene (0.3 v/v).

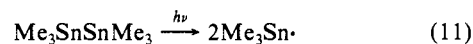
Table IV. Rate Constants (at 300 K) and Arrhenius Parameters for the Reactions of Alkyl Radicals with Carbon Tetrachloride

R·	2k ₅ /k ₁ , M ⁻¹	log (A ₅ /A ₁)	E ₁ - E ₅ , kcal mol ⁻¹	k ₁ , ^a M ⁻¹ s ⁻¹	log (A ₁ /M ⁻¹ s ⁻¹) ^a	E ₁ , ^a kcal mol ⁻¹
<i>n</i> -butyl	1.0 × 10 ⁵	3.0	2.8	5.8 × 10 ⁴	8.6	5.3
cyclopentyl	1.1 × 10 ⁶	4.3	2.4	5.0 × 10 ³	7.3	4.9
<i>tert</i> -butyl	2.0 × 10 ⁵	3.7	2.2	3.1 × 10 ⁴	7.9	4.7

^aTaking 2k₅ = 5.8 × 10⁹ M⁻¹ s⁻¹ at 300 K (ref 14) and E₅ = 2.5 kcal mol⁻¹ by comparison with solvent systems of similar viscosity: Schuh, H.-H.; Fischer, H. *Helv. Chim. Acta* **1978**, *61*, 2130.

While it gave the necessary qualitative information, it failed in a quantitative sense because the initiation process did not provide a clean source of $\dot{\text{C}}\text{Cl}_3$.

Bromotrichloromethane absorbed strongly at the photolysis wavelengths so that reactions 11–14 represent the important initiation steps. However, the presence of trimethyltin chloride and bromodichloromethane imply the incursion of reaction 15 as a complicating factor. While product yields suggested that 15 was a minor reaction, its presence invalidated a quantitative kinetic analysis.



When 1,4-cyclohexadiene was the substrate, there were substantial yields of chloroform but very low yields of hexachloroethane. Despite the difficulties with the initiation steps, the result clearly shows that, in this case, reaction 2 was efficient and reaction 1 was rate limiting.

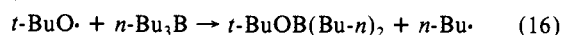
For toluene, the combined yields of CHCl_3 and CHBrCl_2 were only ca. 25% of those for Me_3SnCl and Me_3SnBr , implying that reaction 2 had only moderate efficiency in this instance. Quantitative analysis was not possible in view of difficulties with the initiation process and because the products, bromotoluene and hexachloroethane, had essentially identical retention times in GC analysis on capillary columns.

Taken as a whole, the product studies clearly demonstrate that thermochemistry dictates the relative efficiencies of reactions 1 and 2. Table III shows the heats of these reactions for the substrates investigated. The reactions are slow when thermoneutral but become more efficient when exothermic by >8 kcal mol⁻¹.

Kinetic EPR Measurements

A simple kinetic EPR technique was used to measure k_1 for $\text{R}\cdot = n\text{-Bu}\cdot$, $c\text{-C}_5\text{H}_9\cdot$, and $t\text{-Bu}\cdot$. In this approach, alkyl radicals were generated in the presence of carbon tetrachloride in the cavity of the spectrometer so that both $\text{R}\cdot$ and $\dot{\text{C}}\text{Cl}_3$ could be detected and their concentrations measured.

Alkyl radicals ($\text{R}\cdot = \text{cyclopentyl}$ or *tert*-butyl) were generated by direct photolysis of mixtures of the hydrocarbon (RH) and di-*tert*-butyl peroxide (1:1 v/v) in the EPR cavity. In the presence of appropriate amounts of carbon tetrachloride (0.5–0.9 M), the spectra of $\text{R}\cdot$ and $\dot{\text{C}}\text{Cl}_3$ were observed simultaneously. The experiments were always carried out with a Pyrex filter in the light beam (cut-off 316 nm) to prevent direct photolysis of the carbon tetrachloride. Furthermore, the samples were often flowed continuously through the cavity of the EPR spectrometer to avoid problems associated with sample depletion. The *n*-butyl radical could obviously not be generated by the above route from its parent hydrocarbon and was therefore produced by photolysis of mixtures containing tri-*n*-butylborane and di-*tert*-butyl peroxide (reactions 6 and 16).



The steady-state radical concentrations generated in the EPR approach (ca. 10⁻⁷ M) were ca. 2 orders of magnitude higher than those obtained in the preparative studies so that the trichloromethyl radicals were predominantly removed in radical-radical reactions 4 and 5. Chain propagation through reaction 2 was therefore

relatively unimportant under the EPR conditions.

Application of the steady-state approximation to $[\dot{\text{C}}\text{Cl}_3]$ leads to eq 17 with the usual assumption that since reactions 3–5 are diffusion-controlled processes and involve radicals of similar size, then 2k₃ = k₄ = 2k₅.

$$k_1 \frac{[\text{CCl}_4]}{[\cdot\text{CCl}_3]} = \frac{k_2[\text{RH}]}{[\text{R}\cdot]} + 2k_5 \left(\frac{[\cdot\text{CCl}_3]}{[\text{R}\cdot]} + 1 \right) \quad (17)$$

The term in k_2 reflects the fact that some of the trichloromethyl radicals will regenerate $\text{R}\cdot$ via reaction 2. However, it was possible to calculate the extent of this contribution from the measured radical concentrations and the rate constants k_2 determined in the product studies. In fact, contributions from this term were <15% of those from the other terms in the expression and were therefore negligible with respect to the substantial experimental errors inherent in measuring radical concentrations.²¹

Measurements of the concentrations of $\text{R}\cdot$ and $\dot{\text{C}}\text{Cl}_3$ over a range of temperatures led to values of 2k₅/k₁. Individual values of k_1 were obtained by applying literature data for 2k₅ and led to the rate constants and Arrhenius parameters reported in Table IV.

It is difficult to make reliable error estimates for the kinetic EPR data. Errors in double integration of weak signals due to transient radicals are generally high. They are compounded in this case because the EPR spectrum of trichloromethyl consists of broad overlapping lines that interfered with the spectra of the alkyl radicals.²¹ Moreover, literature data²² indicate that when isobutane is used as a substrate ca. 10–15% of the abstraction by *tert*-butoxyl occurs at its methyl groups. While we were unable to detect the spectrum of the resulting radical, this additional species could make a contribution to the experimental error, albeit small compared with those of integration. Realistically, rate constants could be in error by a factor of 3, A factors by 1 log unit, and activation energies by at least 1 kcal mol⁻¹.

Despite these experimental difficulties, the data lead to the firm conclusion that the results obtained in solution are indeed substantially different from those obtained in the gas phase. The value of k_1 obtained for $\text{R} = t\text{-Bu}\cdot$ is close to that measured in solution by a CIDNP technique (4.9 × 10⁴ M⁻¹ s⁻¹).¹² That for *n*-Bu· was higher but similar to the value measured for 2-substituted 2,2-dimethylethyl radicals ($k_1 = 1.4 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$),¹⁵ although in the light of the experimental errors inherent in both experiments, this difference may not be significant.

Summary

Reactions between alkanes and carbon tetrachloride in solution appear to be controlled largely by thermodynamic factors. The propagation steps are rapid when the reactions are exothermic by >8 kcal mol⁻¹ and are slow when they are thermoneutral.

Rate constants for the reaction between trichloromethyl radicals and alkanes, measured in solution, were similar to those in the gas phase. However, those for the reactions of alkyl radicals with carbon tetrachloride were 2–3 orders of magnitude more rapid in solution. The origin of this effect is unclear. It may possibly stem from solvation of a polar transition state or from experimental error.

The solution data appear to be free from major error since results from four independent techniques^{12,13,15} are in reasonable

(21) Errors in measuring $[\dot{\text{C}}\text{Cl}_3]$ are substantial because of the large number of broad spectral lines. See: Hudson, A.; Hussian, H. A. *Mol. Phys.* **1969**, *16*, 199.

(22) Walling, C.; Jacknow, B. B. *J. Am. Chem. Soc.* **1960**, *82*, 6108.

(23) Benson, S. W. "Thermochemical kinetics", 2nd ed.; Wiley Interscience: New York, 1976.

accord. A new experimental approach to the reaction kinetics in the gas phase could therefore eliminate any lingering doubts about the validity of those data and could substantiate the concept of a major solvation effect for the reaction in solution.

Registry No. Cyclopentane, 287-92-3; cyclohexane, 110-82-7; isobutane, 75-28-5; toluene, 108-88-3; 1,4-cyclohexadiene, 628-41-1; trichloromethyl, 3170-80-7; carbon tetrachloride, 56-23-5; cyclopentyl,

3889-74-5; cyclohexyl, 3170-58-9; isobutyl, 4630-45-9; benzyl, 2154-56-5; 2,5-cyclohexadien-1-yl, 21246-79-7; *n*-butyl, 2492-36-6; *tert*-butyl, 1605-73-8.

Supplementary Material Available: Tables of individual rate constants for the reactions of *n*-butyl, cyclopentyl, and *tert*-butyl radicals with carbon tetrachloride (3 pages). Ordering information is given on any masthead page.

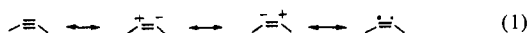
Effect of Bending on the Reactivity of Alkynes: A Semiempirical Study

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Contribution from the Department of Chemistry, University of California, Berkeley, California 94720. Received July 6, 1984. Revised Manuscript Received April 3, 1985

Abstract: The effect of cis bending on the reactivity of alkynes is studied with the semiempirical MNDOC and MNDO methods. The cycloaddition of ethylene to linear and bent acetylene and to benzyne and the addition of water (weak nucleophile) and hydroxide ion (strong nucleophile) to linear and bent acetylene were chosen as model reactions. It was found that only about 20% of the strain energy in the bent alkyne contributes to a direct reduction of the activation barrier for the cycloaddition reaction whereas almost 90% of that strain energy is released in the transition state for nucleophilic additions. The forbidden cycloaddition reaction is very sensitive to electron correlation but the addition of nucleophiles appears to be well described by RHF calculations. The biradicaloid intermediate predicted for the 2 + 2 cycloaddition reaction by limited CI method is highly polarizable and transforms into a closed-shell zwitterion upon interaction with a dipole. Extensive electron correlation treatment (TC-BWEN) removes the biradical as a defined intermediate and changes the reaction surface into a flat plateau supporting Hoffmann's twistyl model. The effect of alkyne bending on the selectivity of addition reactions is discussed.

The reactivity of cyclic alkynes has puzzled organic chemists since the first report on the generation of benzyne by Wittig in 1942.¹ Despite much speculation on the nature of such reactive intermediates no definite proof emphasizing either the closed shell, the zwitterionic, or the biradicaloid structure has been presented.



In several studies the effect of ring size on the reactivity of cyclic alkynes has been examined.¹⁻⁶ Cyclooctyne was found to be the smallest isolable unsubstituted cycloalkyne.³ The most intensively investigated cycloalkyne is benzyne, the chemistry of which has been reviewed.^{2,7} Although there is no experimental evidence for the existence of the smaller cyclopropyne⁸ and cyclobutyne,⁹ convincing evidence for the existence of cyclopentyne,^{3,10} cyclohexyne,³ and cycloheptyne³ has been presented. The tentative assignment of a C≡C stretch frequency at 1930 cm⁻¹ obtained for acenaphthylene, a cyclopentyne derivative, indicates a considerable loss of bond strength for the bent triple bond.¹¹

Table I. Effect of Various Computational Levels on Energy and Geometry of 90° Deformed Acetylene in the MNDO Approximation

computational level	C-C bond, Å	heat of formation, kcal/mol
closed shell	1.302	241.1
2 × 2 CI on c.s. geometry ^a	1.302	218.5
2 × 2 CI optimized	1.372	217.4
3 × 3 CI optimized	1.357	218.8
triplet	1.360	212.2

^a c.s. = closed shell.

Competition reactions have shown that smaller cycloalkynes react faster.³ Force-field calculations predict a strain energy increase of 21 kcal/mol accompanied by a change in angle bending from 172° to 150° at the alkyne position from cyclodecyne to cycloheptyne.⁵ As expected, the ring size determines the degree of bending at the alkyne linkages which correlates with the reactivity. The effect of bending on the electronic structure of alkynes has been studied by ab initio calculations. The investigations show that the LUMO energy drops faster than the HOMO energy rises which explains the increased reactivity of benzyne and other cycloalkynes toward nucleophiles.¹² Although zwitterionic resonance structures have often been postulated to explain the chemistry of bent alkynes,² no convincing evidence for these "ylide" structures has been reported. Stereochemical studies of benzyne-olefin cycloadditions support the formation of biradical intermediates in 2 + 2 reactions with olefins.¹³

In the present study we address the question of how much of the strain energy resulting from alkyne bending is directly

- (1) Wittig, G. *Naturwissenschaften* 1942, 30, 696.
- (2) Hoffmann, R. W. "Dehydrobenzene and Cycloalkynes"; Academic Press: New York, 1967. Krebs, A. In "Chemistry of Acetylenes"; Viehe, H., Ed.; Marcel Dekker: New York, 1969. LeNoble, W. J. "Highlights of Organic Chemistry"; Marcel Dekker: New York, 1974. Greenberg, A.; Liebmann, J. F. "Strained Organic Compounds"; Academic Press: New York, 1978; p 133. Wittig, G. *Pure Appl. Chem.* 1963, 7, 173.
- (3) Nakagawa, M. In "The Chemistry of the Carbon-Carbon Triple Bond"; Patai, S., Ed.; Wiley: New York, 1978. Montgomery, L.; Roberts, J. D. *J. Am. Chem. Soc.* 1960, 82, 4750. Wittig, G.; Wenlich, J.; Wilson, E. *Chem. Ber.* 1965, 98, 458. Gassman, P.; Gennick, I. *J. Am. Chem. Soc.* 1980, 102, 6863.
- (4) Montgomery, L. K.; Applegate, L. E. *J. Am. Chem. Soc.* 1967, 89, 5305.
- (5) Allinger, N. L.; Meyer, A. Y. *Tetrahedron* 1975, 31, 1807.
- (6) Schmidt, H.; Schweig, A.; Krebs, A. *Tetrahedron Lett.* 1974, 16, 1471.
- (7) Bunnett, J. F. *J. Chem. Educ.* 1961, 38, 278. Wittig, G. *Angew. Chem., Int. Ed. Engl.* 1961, 4, 731.
- (8) Saxe, P.; Schaefer, H. F. *J. Am. Chem. Soc.* 1980, 102, 3239.
- (9) Fitzgerald, G.; Saxe, P.; Schaefer, H. F. *J. Am. Chem. Soc.* 1983, 105, 690.
- (10) (a) Fitjer, L.; Kliebisch, U.; Wehle, D.; Modaressi, S. *Tetrahedron Lett.* 1982, 23, 1661. (b) Fitjer, L.; Modaressi, S. *Ibid.* 1983, 24, 5495.

- (11) Chapman, O. L.; Ganjo, J.; West, P. R.; Regitz, M.; Mass, G. *J. Am. Chem. Soc.* 1981, 103, 7033.
- (12) Strozier, R. W.; Carmella, P.; Houk, K. N. *J. Am. Chem. Soc.* 1979, 101, 1340. Rondan, N. G.; Domelsmith, L. N.; Houk, K. N. *Tetrahedron Lett.* 1979, 35, 3237.
- (13) Bowne, A. T.; Christopher, T. A.; Levin, R. H. *Tetrahedron Lett.* 1976, 46, 4111. O'Leary, M. A.; Stringer, M. B.; Wege, D. *Aust. J. Chem.* 1978, 31, 2003. Leitich, J. *Tetrahedron Lett.* 1980, 21, 3025.