Table IV. Rate Constants for the Reaction of Ozone with Olefins $RC_6H_4CH{=}CH_2$ in Carbon Tetrachloride Solution

R	Temp, °C ± 0.1° 5	15	25	35
p-CH_3	1.32 ± 0.15	2.81 ± 0.53	5.29 ± 0.37	10.00 ± 1.30
H	0.90 ± 0.05	1.74 ± 0.10	3.64 ± 0.36	6.65 ± 0.90
p-Cl	0.52 ± 0.05	1.09 ± 0.16	2.25 ± 0.22	3.98 ± 0.58
m-Cl	0.41 ± 0.04	0.87 ± 0.10	1.70 ± 0.19	3.14 ± 0.28
m-NO_2	a	0.44 ± 0.07	0.84 ± 0.06	1.39 ± 0.15

[a] Rate constant too low to be determined.

solution (approximately 13.0 kcal/mol). Owing to the experimental limitations, it was not possible to show a distinct trend of decreasing activation energies for the more electron-releasing substituent group in the ring-substituted styrenes.

Due to the uncertainties of the values for the activation energies, the entropy change accompanying the ozone attack can only be given as a rough approximation. The value of 18.4 ± 1.8 eu which can be calculated for all the olefins from the data presented in Table IV is similar to the value determined (21 ± 2 eu) for the polyalkylbenzenes in carbon tetrachloride solution.

The influence of the ring substituents on the rate constants can easily be interpreted in terms of Hammett's relationship 4[19] where k_0 is the rate constant for styrene.

$$\log k = \log k_0 + \rho\sigma \qquad (4)$$

Figure 3 indicates that the experimental results presented in Table IV are satisfactorily represented by eq 4, with $\rho = -0.91 \pm 0.03$. The slopes of the Hammett plots, *i.e.*, ρ, do not appear to differ significantly at temperatures between 5 and 35°. However, because of the uncertainties due to experimental limitations in the measurements of k, it should not be inferred, from these data, that the ρ values are necessarily independent of temperature.[20]

However, the satisfactory agreement of eq 4 with the experimental k values indicates, unambiguously, that electron-releasing substituents favor ozone attack on the carbon–carbon double bond, whereas electron-withdrawing substituents result in a lowering of the rate constant and hence reduce the possibility of ozone attack. It may thus be concluded that the ozone attack takes place according to an electrophilic process.

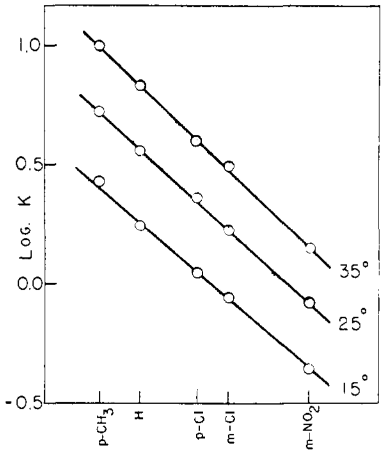


Figure 3. Variation of log k with Hammett's substituent constants at various temperatures.

Acknowledgment. The financial support given by the National Research Council of Canada is gratefully acknowledged.

---

[19] L. P. Hammett, *J. Amer. Chem. Soc.*, **59**, 96 (1937); *Trans. Faraday Soc.*, **34**, 156 (1938); "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940.

[20] It appears nevertheless that ρ is not inversely proportional to T as anticipated by Hammett's ρ–T interrelationship.

Reactions of Dichlorocarbene with Olefins. Temperature Dependence of Relative Reactivities

P. S. Skell and M. S. Cholod

Contribution from the Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802. *Received May 9, 1969*

Abstract: Relative rates of addition of CCl_2 to olefins were determined between 0 and −80°. Relative olefin reactivities were found to vary with temperature, but were independent of the method of CCl_2 generation. Activation parameters were determined for the addition reaction. The olefin–CCl_2 addition mechanism and the relation of CCl_2 to other electrophilic species are discussed.

The chemistry of dichlorocarbene has had much attention during the past 15 years. Methods are available for generation of this carbene over the temperature range −100 to 1500°. Nonetheless reports of the effect of temperature on this (and other) carbene reactions are scarce. It was of interest to learn if activation enthalpies for additions to olefins were consistent with the early suggestions that carbenes were electrophilic species whose reactivities were moderated by resonance stabilization.[1,2]

Doering and coworkers[3] found that photolysis of diazomethane in a number of hydrocarbons at −75 and +15° gave essentially the same mixture of C–H insertion products suggestive of statistical C–H insertion. Skell and Plonka[4] found that carbenes from deoxygenation of carbonyl compounds by deposition with C_1 at −196° gave essentially the same intramolecular product mixtures (olefins and cyclopropanes) as does decomposition of the corresponding diazo compounds at 100–200°. Similarly, photolyses of diazirines at −196° give results similar to those for thermal decomposition at 100–200°.[5]

In their study of CTF produced by the reaction of recoil tritium atoms with CH_2F_2, Tang and Rowland[6] allowed CTF to react competitively with *trans*-2-butene and ethylene at 40, 22, and −12°. A small temperature dependence of relative reactivities for addition was observed which was attributed to an activation energy difference, $E(C_2H_4) - E(C_4H_8) = 0.77$ kcal/mole.

Mitsch[7] measured the relative rates of addition of CF_2 to a number of olefins at 36 and 91°. The CF_2 was generated by photolysis of 3,3-difluorodiazirine. The major factor determining the relative rates was the difference in E_{act}, for example, tetramethylethylene (standard) 0.0 kcal/mole, trimethylethylene 0.87 kcal/mole, isobutylene 2.88 kcal/mole, *trans*-2-butene 3.96 kcal/mole, and propene 5.20 kcal/mole. This is the selectivity expected for an electrophilic reagent. Cvetanović[8] found similar but smaller relative activation energies for ground-state oxygen atom reactions with olefins.

Dichlorocarbene derived from *t*-BuOK and chloroform[9] showed relative reactivities in reactions with olefins which paralleled those found earlier[1] for CBr_2, epoxidation and ionic bromination of olefins, placing each of these reagents in the same category, electrophilic. There is one report of the effect of temperature on relative reactivities. Nefedov and Shafran[10] compared reactivities of three 1-substituted cyclohexenes (CH_3, Cl, and CH_3CO substituents) with cyclohexene toward the CCl_2 intermediate generated by some or all of the following: Cl_3CCO_2Na and $PhHgCCl_3$ thermolysis at ∼80°, Li + $CHCl_3$ at ∼10°, *t*-BuOK + $CHCl_3$ at −10 to −15°, MeLi + $CHCl_3$ at −20°, and MeLi + $BrCCl_3$ at −60°. The relative reactivity of a given olefin pair was found to be independent of both the CCl_2 source as well as the temperature of reaction.

The identity of the reactive intermediates of dichlorocyclopropanation has been recognized as a problem: is it CCl_2 or a complex of CCl_2, a carbenoid? This matter is settled in the preceding paper,[11] free CCl_2 being the sole intermediate for olefin addition reactions.

Results

Some practical methods for generation of dichlorocarbene at various temperatures are summarized in Table I.

Table I. Methods of Dichlorocarbene Generation

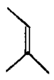
Method	Temp, °C	Ref
$CHCl_3$, Δ	1500	*a*
Cl_3SiCCl_3, Δ	250	*b*
$CHCl_3 + (CH_2)_2O + X^-$	150	*c*
Cl_3CCO_2Na, Δ	80–100	*d*
$PhHgCCl_2Br$, Δ	80	*e*
$PhHgCCl_2Br + I^-$	25	*f*
$CHCl_3$ + *t*-BuOK	≤0	*g*
$CHCl_3$ + BuLi, THF	−80 to 0	*h,i*
$CHCl_3$ + BuLi·TMEDA	−80 to −30	*j*
$CHCl_3$ + BuLi, Et_2O	−110 to 0	*k*

[a] L. D. Wescott and P. S. Skell, *J. Am. Chem. Soc.*, **87**, 1721 (1965). [b] W. I. Bevan, R. N. Haszeldine, and J. C. Young, *Chem. Ind.* (London), 789 (1961). [c] P. Weyerstahl, D. Klamann, C. Finger, F. Neidel, and J. Buddrus, *Chem. Ber.*, **100**, 1858 (1967). [d] W. M. Wagner, H. Kloosterziel, and S. van der Ven, *Rec. Trav. Chim. Pays-Bas*, **80**, 740 (1961). [e] D. Seyferth, J. M. Burlitch, and J. K. Heeren, *J. Org. Chem.*, **27**, 1491 (1962). [f] D. Seyferth, M. E. Gordon, J. Y-P. Mui, and J. M. Burlitch, *J. Am. Chem. Soc.*, **89**, 959 (1967). [g] See ref 9. [h] D. F. Hoeg, D. I. Lusk, and A. L. Crumbliss, *J. Am. Chem. Soc.*, **87**, 4142 (1965). [i] G. Köbrich, K. Flory, and R. H. Fischer, *Chem. Ber.*, **99**, 1793 (1966). [j] This work. [k] W. T. Miller and D. M. Whalen, *J. Am. Chem. Soc.*, **86**, 2089 (1964).

The tetramethylethylenediamine (TMEDA) complex of $LiCCl_3$ had not been described previously. It is made by the reaction of monomeric BuLi·TMEDA[12] with either chloroform or bromotrichloromethane in a hydrocarbon solvent at low temperature (eq 1).

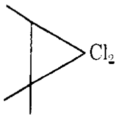
$$\mathrm{BuLi\cdot TMEDA + CXCl_3 \xrightarrow{-108^\circ} TMEDA\cdot LiCCl_3 + BuX} \quad (1)$$

TMEDA·$LiCCl_3$ was thus formed as a white solid, slightly soluble in isopentane, and stable at temperatures below −80°, even in the presence of olefins. The behavior of TMEDA·$LiCCl_3$ with respect to temperature is similar to that of $LiCCl_3$ generated in tetrahydrofuran;[13,14] it decomposes to a brown-black solid material at −60° just as reported for the THF reagent. Good yields of dichlorocyclopropanes have been obtained by stirring TMEDA·$LiCCl_3$ with olefin at −78° for extended periods of time (eq 2); 1,1-dichloro-2,2,3-trimethylcyclopropane was formed from



+ TMEDA·$LiCCl_3$ ⟶

TMEDA·LiCl +



(2)

trimethylethylene in 75% yield in 1 hr at −78°. Smaller conversions (0–20%) were obtained with shorter reaction times.

---

[1] P. S. Skell and A. Y. Garner, *J. Am. Chem. Soc.*, **78**, 5430 (1956).
[2] J. Hine and S. J. Ehrenson, *ibid.*, **80**, 824 (1958).
[3] W. von E. Doering, R. G. Buttery, R. G. Laughlin, and N. Chaudhuri, *ibid.*, **78**, 3224 (1956).
[4] P. S. Skell and J. H. Plonka, unpublished results.
[5] P. S. Skell and L. S. Wood, unpublished results.
[6] Y-N. Tang and F. S. Rowland, *J. Am. Chem. Soc.*, **89**, 6420. (1967).
[7] R. A. Mitsch, private communication.
[8] R. J. Cvetanović, *J. Chem. Phys.*, **33**, 1063 (1960); *Can. J. Chem.*, **38**, 1678 (1960).
[9] W. von E. Doering and W. A. Henderson, Jr., *J. Am. Chem. Soc.*, **80**, 5274 (1958).
[10] O. M. Nefedov and R. N. Shafran, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 538 (1965).
[11] P. S. Skell and M. S. Cholod, *J. Am. Chem. Soc.*, in press.
[12] A. W. Langer, Jr., *Trans. N. Y. Acad. Sci.*, **27**, 741 (1965).
[13] See Table I, footnote *h*.
[14] See Table I, footnote *i*.

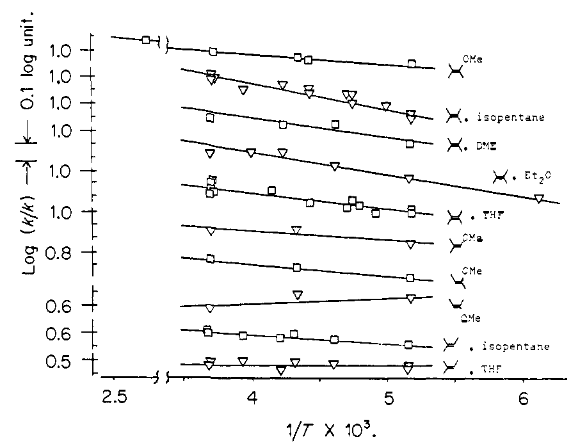


Figure 1. Arrhenius plots (relative to isobutylene).

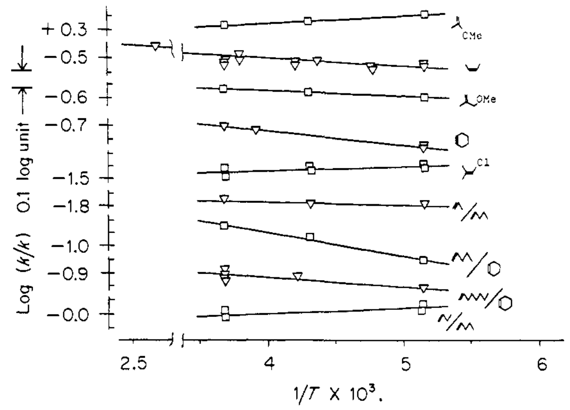


Figure 2. Arrhenius plots (relative to isobutylene except where noted).

Olefin competition reactions were run at low temperatures by generating a CCl_2 precursor in a suitable solvent containing an olefin mixture of known composition. The reaction was allowed to proceed to small conversion of the olefin to dichlorocyclopropanes, at which time a quenching agent, consisting of 1 part of methanol to 1 part of acetic acid (1:1 methanol–water for methoxy olefins), was added dropwise to destroy the balance of CCl_2 precursor. Competitions were run in which CCl_2 was generated by the TMEDA·$LiCCl_3$ method and by the reaction of butyllithium and either chloroform or bromotrichloromethane in various solvents (THF, diethyl ether, and 1,2-dimethoxyethane). Use of diethyl ether as solvent provided reaction at temperatures as low as −110°. Dichlorocarbene generation from $CHCl_3$ + *t*-BuOK was employed at temperatures between 0 and −20°, but at lower temperatures the reaction was too slow to be of utility. Extent of olefin reaction was generally between 1 and 15% theoretical; relative rates were calculated by the method of Skell and Garner.[1] Probable error in log k_1/k_2 values has been estimated on the basis of reliability in the determination of product and olefin ratios to be less than ±0.04.

Table II. Olefin Relative Reactivities

Olefin	Log *k*, 0°	Log *k*, −78°
2-Methoxy-3-methyl-2-butene[a]	1.00	0.89
Tetramethylethylene[d]	1.02	0.74
Tetramethylethylene[b]	0.93	0.75
Tetramethylethylene[c]	0.90	0.67
Tetramethylethylene[a]	0.88	0.72
1-Methoxy-2-methylpropene[a]	0.89	0.80
cis-2-Methoxy-2-butene[a]	0.75	0.62
trans-2-Methoxy-2-butene[a]	0.60	0.68
Trimethylethylene[d]	0.62	0.52
Trimethylethylene[a]	0.48	0.48
2-Methoxypropene[a]	0.30	0.38
Isobutylene	[0.00]	[0.00]
cis-2-Butene[a,d,e,f]	−0.50	−0.58
2-(Methoxymethyl)propene[a]	−0.55	−0.60
Cyclohexene[a]	−0.72	−0.86
1-Chloro-2-methylpropene[a]	−1.47	−1.40
Propene[a]	−1.42	−1.80
1-Butene[a]	−1.54	−1.99
1-Pentene[a]	−1.56	−1.98
1-Octene[d−f]	−1.61	−1.92

[a] BuLi + $CHCl_3$, THF solvent. [b] BuLi + $CHCl_3$, DME (1,2-dimethoxyethane) solvent. [c] BuLi + $CHCl_3$, Et_2O solvent. [d] BuLi·TMEDA + $CHCl_3$, isopentane solvent. [e] *t*-BuOK + $CHCl_3$, isopentane solvent. [f] Relative rates independent of solvent.

Arrhenius plots for the various olefin pairs are shown in Figures 1 and 2, and the relative reactivities are listed for 0 and −78° in Table II. Table III list the activation parameters, the $\Delta\Delta H^{\neq}$ and $\Delta\Delta S^{\neq}$ obtained from Arrhenius plots of the data. These are the most extensive reactivity and activation data compiled for an electrophilic reagent. Probable error in the $\Delta\Delta H^{\neq}$ and $\Delta\Delta S^{\neq}$ values estimated from the accuracy of the log k/k values are ±0.25 kcal/mole and ± 1.0 eu, respectively.

Relative rates of CCl_2 addition to olefins were independent of the absolute olefin concentrations; *k*(1-octene)/*k*(cyclohexene) remaned constant for total olefin concentration ranging from ~10^{-2} to ~7 *M* (see Table VI). The relative rates showed no variation when the CCl_2 was generated in a homogeneous system using butyllithium plus chloroform in THF or in a heterogeneous system using *t*-BuOK and chloroform in isopentane solvent. Solvent has little effect on the relative rates of reaction of the less reactive olefins; *k*(*cis*-2-butene)/*k*(isobutylene) values were the same, within experimental error, regardless of solvent. Trimethylethylene and tetramethylethylene reacted 25% faster in isopentane than in the other solvents (Et_2O, DME, THF) at 0°; the rates in the various solvents converged at lower temperature.

Discussion

Electrophilic Character of CCl_2. The order of olefin reactivities indicates that dichlorocarbene acts as an electrophile both at 0 and −78°. The simple hydrocarbon olefins (tetramethylethylene, trimethylethylene, isobutylene, *cis*-2-butene, propylene, 1-butene, and 1-pentene) reactivities correlate with the Taft polar–steric relation,[15] $\log (k/k_0) = \rho^*\sigma^* + \delta E_s$, where $\rho^* \sim -4.3$ and $\delta \sim 1.0$ indicative of an electrophilic reagent; the corresponding values determined by DuBois[16] for bromination of olefins are $\rho^* = -5.43$ and $\delta = 0.96$. Moss and Mamantov[17] showed that the influence of substituent size for $RCH{=}CH_2$ (R = Et, *i*-Pr, *t*-Bu) on the relative rates of CCl_2 addition are also correlated by a value of $\delta = 1.0$.

(15) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc., New York, N. Y., 1956, p 556 ff.

(16) G. Mouvier and J. E. DuBois, *Bull. Soc. Chim. France*, 1441 (1968).

(17) R. A. Moss and A. Mamantov, *Tetrahedron Lett.*, 3425 (1968).

Table III. Activation Parameters

Olefin	$\Delta\Delta F^{\ddagger}$ (0°), kcal/mole	$\Delta\Delta F^{\ddagger}$ (−78°), kcal/mole	$\Delta\Delta H^{\ddagger}$, kcal/mole	$\Delta\Delta S^{\ddagger}$, eu	273° × $\Delta\Delta S^{\ddagger}$, kcal/mole
2-Methoxy-3-methyl-2-butene[a]	−1.26	−0.80	+0.30	5.72	−1.56
Tetramethylethylene[d]	−1.28	−0.67	+0.89	7.95	−2.17
Tetramethylethylene[b]	−1.17	−0.68	+0.58	6.48	−1.77
Tetramethylethylene[c]	−1.13	−0.60	+0.70	6.71	−1.83
Tetramethylethylene[a]	−1.10	−0.65	+0.53	5.97	−1.63
cis-2-Methoxy-2-butene[a]	−0.94	−0.57	+0.43	5.02	−1.37
trans-2-Methoxy-2-butene[a]	−0.75	−0.62	−0.28	1.72	−0.47
Trimethylethylene[d]	−0.78	−0.47	+0.26	3.81	−1.04
Trimethylethylene[a]	−0.60	−0.43	+0.07	2.46	−0.67
2-Methoxypropene[a]	−0.38	−0.34	−0.23	0.55	−0.15
Isobutylene	[0.00]	[0.00]	[0.00]	[0.00]	[0.00]
cis-2-Butene[a,d–f]	0.63	0.57	+0.29	−1.25	+0.34
2-(Methoxymethyl)propene[a]	0.69	0.54	+0.14	−2.02	+0.55
Cyclohexene[a]	0.90	0.77	+0.14	−2.78	+0.76
1-Chloro-2-methylpropene[a]	1.84	1.26	+0.22	−5.94	+1.62
Propene[a]	1.78	1.62	+1.19	−2.16	+0.59
1-Butene[a]	1.94	1.79	+1.41	−1.96	+0.53
1-Pentene[a]	1.96	1.78	+1.31	−2.38	+0.65
1-Octene[d–f]	2.02	1.72	+0.97	−3.85	+1.05

[a] BuLi + $CHCl_3$, THF solvent. [b] BuLi + $CHCl_3$, DME solvent. [c] BuLi + $CHCl_3$, Et_2O solvent. [d] BuLi·TMEDA + $CHCl_3$, isopentane solvent. [e] *t*-BuOK + $CHCl_3$, isopentane solvent. [f] Relative rates independent of solvent.

Comparison of free energies of activation for the dichlorocarbene–olefin reactions at 0° and other electrophile–olefin systems are shown in Figure 3. In general, good straight-line correlations were obtained; the slopes are shown in Table IV. A qualitative comparison of the reagents according to the magnitude of the slopes indicates that the reagents increase in selectivity in the order CH_2 < O atoms < CBr_2 < $(CH_3)_2C{=}C{=}C$: < CCl_2 < CH_3CO_3H < CFCl < CF_2 ~ Br_2. This can be interpreted as the order of decreasing electrophilicity (*vide infra*). The increase of selectivities for CBr_2 < CCl_2 < CF_2 is in accord with the early suggestions, and is correlated to the abilities of the halogen atoms to supply electrons to the electron-deficient carbene carbon atom,[1,2] thus stabilizing the carbene.

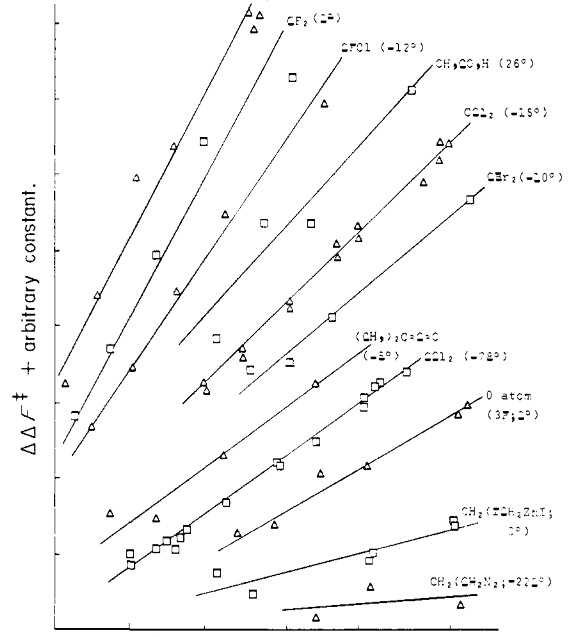


Figure 3. Linear free energy plots.

Table IV. Linear Free Energy Slopes

Olefin reaction partner	Slope[a]	Ref
CH_2, 225°	~0.1	*b*
ICH_2ZnI, 0°	0.25	*c*
O atoms, 25°	0.60	*d*
:CCl_2, −78°	0.74	*e*
$(CH_3)_2C{=}C{=}C$:, −5°	0.77	*f*
:CBr_2, −10°	0.82	*g*
:CCl_2, −15°	0.99	*e,h*
:CCl_2, 0°	(1.00)	*e*
CH_3CO_3H, 26°	1.11	*i*
:CFCl, −12°	1.51	*j*
Br_2, 25°	1.90	*k*
:CF_2, 0°	1.92	*l*

[a] $(\Delta\Delta F^{\ddagger})_{x,t°}$ = slope $(\Delta\Delta B^{\ddagger})$ CCl_2, 0°. [b] H. S. Skovronek, Ph.D. Thesis, The Pennsylvania State University, 1961. [c] E. P. Blanchard and H. E. Simmons, *J. Am. Chem. Soc.*, **86**, 1337 (1964). [d] See ref 8. [e] This work. [f] H. D. Hartzler, *J. Am. Chem. Soc.*, **83**, 4997 (1961). [g] See ref 1. [h] See ref 9. [i] D. Swern, *J. Am. Chem. Soc.*, **69**, 1692 (1947). [j] R. A. Moss and R. Gerstl, *Tetrahedron*, **23**, 2549 (1967); *J. Org. Chem.*, **32**, 2268 (1967). [k] J. E. DuBois and G. Mouvier, *Bull. Soc. Chim. France*, 1426 (1968). [l] See ref 7.

The concept of electrophilicity or degree of electrophilicity is in common parlance without a precise definition. The concept relates in principle to the freeness of a vacant p orbital, and relates to experiment by an increasing rate of reaction with increasing nucleophilicity of a series of reagents. For the present only relative rates are available, somewhat clouding the use of the concept. From theory, CH_2 has a freer p orbital than CCl_2, and thereby CH_2 would be classed the more electrophilic. With olefins of increasing alkyl substitution, as test reagents, it is found that CCl_2 is more selective (a greater spread of rates). This inverse relation between selectivity and electrophilicity is rationalized by a decrease in $\Delta\Delta H^{\ddagger}$ with a decrease in $\Delta H^{\ddagger}$ (Figure 4).

A strongly electrophilic reagent does not spread the olefin rates and thus the feature which distinguishes electrophiles from nonelectrophiles tends to vanish with increasing electrophilicity of the reagent.

Ignoring this confusion, the degree of electrophilicity of a reagent is correlated inversely with the selectivity,

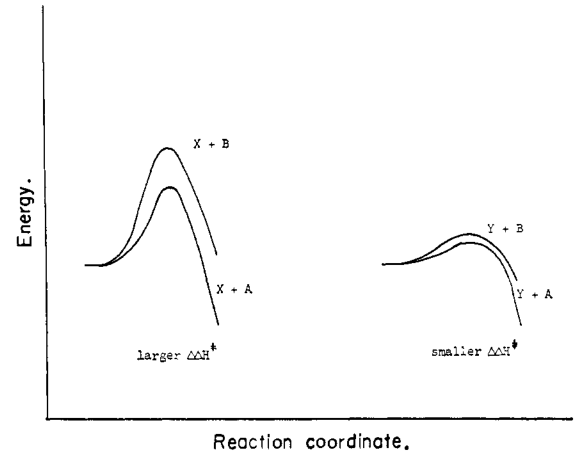


Figure 4.

the slopes of Figure 2; the smaller slope corresponds to the more electrophilic reagent.

Mechanism

Relative rates of acid-catalyzed hydration[18,19] are propylene 1.00, *cis*-2-butene 0.71, *trans*-2-butene 1.68, isobutylene 10^3–10^4, and trimethylethylene 10^3–10^4. Olefins capable of forming tertiary carbonium ions react three to four powers of ten faster than olefins which can only form secondary carbonium ions.

It should be noted that the electrophilic processes listed in Table IV differ in two respects: (1) the spread of rates is smaller, and (2) olefin reactivity increases with increasing alkyl substitution regardless of their distribution about the double bond.

The lack of a parallel in the rates of dihalocarbene–olefin additions and alkene hydration suggests that the carbene reaction does not proceed through an intermediate in which a large positive charge is developed on *one* of the carbon atoms. Thus, two varieties of electrophiles are recognized, those which add to one carbon of the double bond to form carbonium ions and those which add to both atoms, bridging electrophiles.

Comparison of olefin reactivity toward CCl_2 with the olefin ionization potentials (Figure 5), or more simply the number of alkyl substituents on the carbon–carbon double bond (Figure 6), does show a better correlation. Since isobutylene is more reactive than 2-butene it becomes necessary to consider an unsymmetrical bridging conferring upon the intermediate some carbonium ion character. The over-all olefin reactivities appear to be determined primarily by the polarizability of the olefin along the π axis, and to a lesser extent by the ability of the olefins to form stabilized "carbonium ion" intermediates.

A mechanism consistent with these considerations is one in which the vacant p orbital of the singlet carbene approaches the olefin along the π axis closer to the least substituted carbon atom to form a loose charge-transfer type complex which then collapses with rotation of the CCl_2 group to the product dichlorocyclopropane (Scheme I). The transition state is polarized with the olefin electron poor and the carbene electron rich.

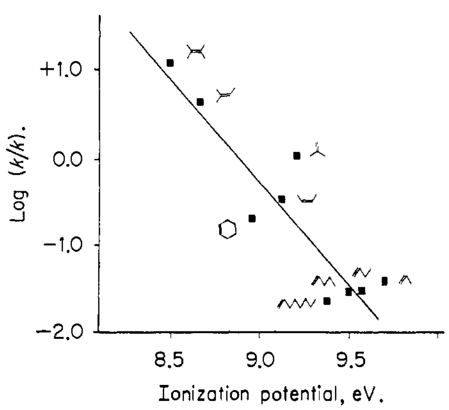


Figure 5. Relative reactivity *vs.* ionization potential. Tetramethylethylene I.P. is from J. Collin and F. P. Lossing, *J. Am. Chem. Soc.*, **81**, 2064 (1959); all others are from K. Watanabe, T. Nakayama, and J. Mottle, *J. Quant. Spectrosc. Rad. Trans.*, **2**, 369 (1962)).

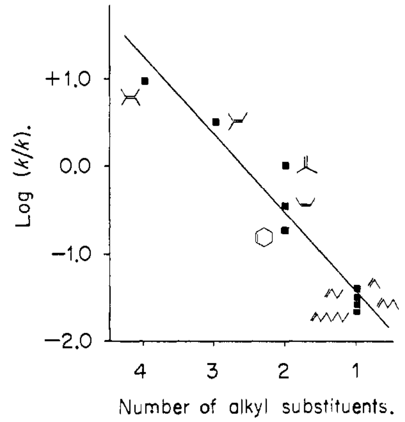
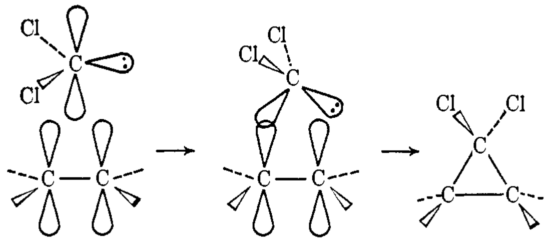


Figure 6. Relative reactivity *vs.* number of alkyl substituents.

This mechanism was first proposed by Skell and Garner for CBr_2 additions. Hoffmann has proposed[20]

Scheme I



essentially the same and focused on detail not considered earlier, mainly the precise location of the carbene carbon with reference to the perpendicular bisector of the carbon–carbon double bond. He finds displacement to the right of the bisector gives a slightly more stable structure. However, whether the approach is along the bisector or to the right of it, there is negative charge transfer to the approaching carbene with significant depletion from *both* carbon atoms of the double bond.

Activation Parameters

The activation parameters for CCl_2–olefin reactions were determined from the present data and are shown in Table III. For any given olefin pair straight-line plots were obtained for $\Delta\Delta F^{\ddagger}$ *vs.* $1/T$. The lines were inde-

---

(18) P. Riesz, R. W. Taft, Jr., and R. H. Boyd, *J. Am. Chem. Soc.*, **79**, 3724 (1957).

(19) P. D. Bartlett and G. D. Sargent, *ibid.*, **87**, 1297 (1965).

(20) R. Hoffmann, *ibid.*, **90**, 1475 (1968).

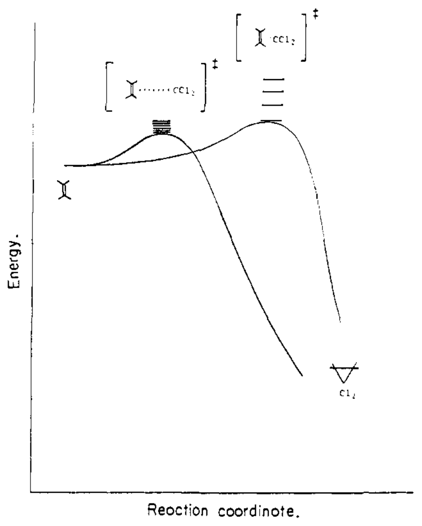


Figure 7.

pendent of the method used to generate the CCl_2 and solvent except for trimethylethylene and tetramethylethylene (*vide supra*) which showed solvent dependences (~0.3 kcal/mole variation in $\Delta\Delta H^{\ddagger}$).

Although the $\Delta\Delta F^{\ddagger}$ (Table III) vary with structure in an understandable manner, there appears to be little correlation between olefin reactivity and the activation enthalpy. For the majority of the olefins the $\Delta H^{\ddagger}$ differ by little more than the experimental uncertainty. The temperature-independent part, $\Delta S^{\ddagger}$, parallels the rates and, in addition, it is the dominant factor. In most instances $T\Delta S^{\ddagger} > \Delta H^{\ddagger}$; the least reactive olefins, the 1-alkenes, are the exceptions.

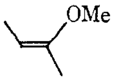
Since the system is $\Delta S^{\ddagger}$ dominated, the following interpretation is attractive. The more reactive olefins have a transition state with larger separation of CCl_2 and olefin than do the less reactive olefins. A larger separation implies weaker binding, lower frequency vibrations along the contracting reaction axis, more closely spaced vibrational states, a greater use of these states in the transition state saddle, and consequently a more positive $\Delta S^{\ddagger}$. Conversely, the tighter transition state of the less reactive olefins has wider spaced levels and fewer are occupied; thus a less positive (more negative) $\Delta S^{\ddagger}$ (Figure 7).

A corrolary to this hypothesis, relating to electrophilicity, is increasing electrophilicity of the reagent shifts the free energy curve toward looser, reactantlike transition state. Thus, the strongly electrophilic reagents (small slopes of Figure 2) would be $\Delta S^{\ddagger}$ dominated. At the other extreme a weakly electrophilic reagent (large slope) would go to a tight transition state and be $\Delta H^{\ddagger}$ dominated. The remarkable feature would be that the transition between $\Delta S^{\ddagger}$- and $\Delta H^{\ddagger}$-dominated reaction types occurs with compensations that maintain the good $\Delta F^{\ddagger}$ correlations of Figure 2.

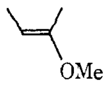
This activation parameter–reactivity correlation, although appealing, is contingent on the ability of the Arrhenius equation to separate effectively $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ terms of the small magnitude encountered here. Should the Arrhenius equation prove to be too crude a tool to effect this separation,[21] meaningful detailed interpretation of the $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ values is obviously impossible.

Experimental Section

Olefins. Hydrocarbon olefins, isopropenyl methyl ether, and 1-chloro-2-methylpropene, were obtained from commercial sources. Methallyl methyl ether was prepared *via* a Williamson synthesis utilizing the sodium salt of methallyl alcohol and methyl iodide; 2-methoxy-3-methyl-2-butene (bp 95–96°) was obained from pyrolysis of the corresponding dimethyl ketal.[22] Pyrolysis of isobutyraldehyde dimethyl acetal afforded 1-methoxy-2-methylpropene[23,24] (bp 70–72°). The isomeric 2-methoxy-2-butenes were obtained by dehydrohalogenation of the isomeric 2-bromo-3-methoxybutanes, prepared by reaction of N-bromosuccinimide and a 2-butene in acidic methanol. Starting with *cis*-2-butene, *threo*-2-bromo-3-methoxybutane was obtained which upon dehydrohalogenation yielded *cis*-2-methoxy-2-butene (I), bp 67–69°. *trans*-2-Butene similarly gave the *trans*-2-methoxy-2-butene (II), bp 73–74°.



I



II

Cyclopropanes. Dichlorocyclopropanes listed in Table II were generally prepared through the action of *t*-BuOK on chloroform in the presence of excess olefin at ~0°.[9] When only limited amounts of olefin were available reaction was carried out at ~−55° on a 5–10-mmole scale using butyllithium and chloroform in THF; gas chromatographic separation then afforded the pure dichlorocyclopropanes. Infrared and nmr spectra were in accord with the assigned dichlorocyclopropane structures.

Kinetics. Competition reactions were usually carried out in a 250-ml, three-necked flask equipped with a stirrer and Dry Ice condenser, and maintained under a nitrogen atmosphere. The flask, containing ~45 ml of solvent, 10 mmoles of chloroform, and a quantity (usually 75–100 mmoles) of a known olefin mixture, was cooled to the desired reaction temperature with an external bath. The temperature was monitored by means of an iron–constantan thermocouple in the reaction mixture and maintained ±2° during the reaction period. For competitions using Et_2O, DME, or THF as the solvent, BuLi in hexane was added to the olefin–chloroform–solvent mixtures dropwise at a rate which did not appreciably change the reaction temperature. The molar ratio of BuLi to $CHCl_3$ was always <1.0 and usually <0.5. When isopentane was the solvent BuLi·TMEDA in hexane–isopentane was used in place of the BuLi. BuLi·TMEDA was prepared by stirring equimolar amounts of BuLi and TMEDA together for 10–15 min under a nitrogen atmosphere. After complete addition of BuLi (or BuLi·TMEDA), the reaction mixture was allowed to stir for an additional period of time (usually 30–60 min) before quenching with a 1:1 mixture of methanol–acetic acid (methanol–water when methoxy olefins were used). Product mixtures were washed with water and analyzed for dichlorocyclopropanes by vpc.

Table V. Sample Competition Reactions

Olefin pair	Log *k*/*k*, 0°	Log *k*/*k*, −78°
1-Butene/cyclohexene	−0.78	−1.18
1-Pentene/cyclohexene	−0.85	−1.12
1-Octene/cyclohexene	−0.90	−1.06
Propene/1-pentene	+0.15	+0.18
1-Butene/1-pentene	−0.02	+0.04
1-Chloro-2-methylpropene/1-pentene	+0.09	+0.58
Cyclohexene/isobutylene	−0.72	−0.86
1-Chloro-2-methylpropene/isobutylene	−1.49	−1.43

---

[21] Recognized by a curvature in the Arrhenius plots for the absolute rates of the reactions of CCl_2 with olefins. Dividing one curve by another may cancel this curvature to give a straight line for the resultant relative rate variations with temperature. Nonetheless, the separation into temperature-dependent and temperature-independent terms is chancy.

[22] D. G. Lindsay and C. B. Reese, *Tetrahedron*, 21, 1673 (1965).

[23] M. F. Ansell and B. Gadsby, *J. Chem. Soc.*, 3388 (1958).

[24] M. Farina, M. Paraldo, and G. Bressan, *Chem. Ind.* (Milan), **42**, 967 (1960).

Chromatographic areas were corrected for detector response, and absolute yields of dichlorocyclopropanes were determined by addition of either *m*-xylene or *cis*-decalin as an internal standard. Relative rates were calculated as previously described.[1]

When *t*-BuOK was used as the base the following modifications were made: *t*-BuOK (usually ~10 mmoles) was weighed into the flask under nitrogen, followed by addition of the solvent and olefin mixture. After temperature equilibration an excess of $CHCl_3$ in isopentane was added dropwise, followed by the usual work-up procedure.

Competition results are presented graphically in Figure 1 and values at 0 and −78° are given in Table II. Except for 1-chloro-2-methylpropene and the 1-alkenes all competitions were run using isobutylene as the reference olefin. Table V lists competitions in which olefins other than isobutylene were used as the reference. In Table VI are the results of 1-octene/cyclohexene competitions run at varying total olefin concentration.

Table VI. Olefin Reactivity *vs.* Absolute Olefin Concentration[a]

Total olefin concn, moles/l	Log *k*(1-octene)/*k*(cyclohexene)	Dichlorocyclopropane yield, mmoles
~6.7[b]	−0.93	3.3
3.0[c]	−0.94	3.1
9.0×10^{-2}[c]	−0.86	0.3
9.0×10^{-3}[c]	−0.92	<0.1

[a] Reaction at 0° for 7.5–8.0 hr; 10 mmoles of *t*-BuOK and 12.5 mmoles of $CHCl_3$ were added to olefin mixture. [b] Neat olefin. [c] Isopentane solvent.

Acknowledgment. We acknowledge the financial support of the Air Force Office of Scientific Research.

Calculation and Qualitative Predictions of Mass Spectra. Mono- and *para*-Disubstituted Benzenes

Ian Howe and Dudley H. Williams

Contribution from the University Chemical Laboratory, Cambridge, England.

Received May 21, 1969

Abstract: A classification of the relative ease of fragmentation of substituents in 17 monosubstituted benzenes is drawn up in terms of daughter/parent ($[A^+]/[M^+]$) ion ratios at 18 eV. This order is rationalized with the aid of ionization and appearance potential measurements; the quasi-equilibrium theory calculations show good consistency in most cases with observed $[A^+]/[M^+]$ ratios and metastable ion abundances. A similar order of "ease of fragmentation" of a substituent is drawn up simply in terms of the appearance potential of the daughter ions and is tested in the spectra of *para*-substituted bromobenzenes and anilines. This classification predicts the more abundant daughter ion, which usually swamps the other process except where the two appearance potentials are close. Where a "readily fragmentable group" (*i.e.*, COMe, CO_2Me) is used as the fixed substituent in a series of disubstituted benzenes, the change in the main $[A^+]/[M^+]$ ratio is attributable to the variation in ionization potential and the accompanying change in activation energy E_0. Results are presented to illustrate that the process of lowest appearance potential gives the most abundant "metastable peak."

A feature of recent papers concerned with substituent effects[1-5] has been a more rigorous approach to the factors governing daughter/parent ion ratios. This development has led to a broader understanding of substituent effects measured in terms of ion ratios.

The factors influencing $[A^+]/[M^+]$ ratios at the collector for the reaction $M^+ \rightarrow A^+$ are now established,[1-4] the most important ones being as follows.

1. The rate constant k_A for fragmentation and its variation with internal energy E. These k *vs.* E curves depend on (i) the activation energy E_0 for formation of A^+ and (ii) the frequency factor ν for the fragmentation.
2. The fraction of M^+ ions not having the energy to fragment to A^+. This fraction is larger for a larger difference between ionization potential (I.P.) and appearance potential of A^+ (A.P.) and larger for a smaller electron beam energy, but its exact value is dependent on the internal energy distribution of M^+.
3. Secondary decompositions of A^+ (which influence the intensity of A^+). This problem may be largely alleviated by using low electron beam energies.
4. Competitive decompositions from M^+. In the general case, $[A^+]/[M^+]$ will be dependent on the rates of all competing unimolecular reactions from M^+ and the extent of this dependence is of considerable importance to the discussions in this paper.

Discussion

Monosubstituted Benzenes. Toward a classification and ordering of substituents in terms of relative ease of fragmentation and toward the empirical prediction of the spectra of disubstituted benzenes, we have measured the mass spectra of a number of monosubstituted benzenes at 18 eV. The daughter/parent ion ratios $[A^+]/[M^+]$, together with the I.P. of M^+ and the A.P. of A^+, are listed in Table I.

From the data in Table I, the general trend toward a decrease in $[A^+]/[M^+]$ as A.P. − I.P. is increased is clearly evident.

The quasi-equilibrium theory (QET) of mass spectra[6]

---

(1) I. Howe and D. H. Williams, *J. Am. Chem. Soc.*, **90**, 5461 (1968).

(2) R. G. Cooks, R. S. Ward, I. Howe, and D. H. Williams, *Chem. Commun.*, 837 (1968).

(3) R. G. Cooks, I. Howe, and D. H. Williams, *Org. Mass. Spectrom.*, **2**, 137 (1969).

(4) F. W. McLafferty, *Chem. Commun.*, 956 (1968).

(5) P. Brown, *J. Am. Chem. Soc.*, **90**, 4459 (1968).

(6) H. M. Rosenstock, M. B. Wallenstein, A. L. Wahrhaftig, and H. Eyring, *Proc. Natl. Acad. Sci. U. S.*, **38**, 667 (1952).