

Electrophilic Reactions at Multiple Bonds. I. The Study of Selectivity and the Role of π and σ Complexes in the Addition of Bromine to Alkenes and Alkynes in 1,1,2-Trichlorotrifluoroethane Solution

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Abstract: Competitive rate data were obtained for the addition of bromine to a series of alkenes in 1,1,2-trichlorotrifluoroethane solution at -35° . A considerably smaller range in relative rates was obtained in his study compared with previous data for bromination of similar alkenes in a more polar solvent. This is interpreted as resulting from a change in the position of the highest energy transition state along the reaction coordinate. The data indicate that the earlier, reactant like transition states in the present study are of π complex nature. The proposed π complex mechanism accounting for substrate selectivity is in accord with comparison of the heats of formation of the corresponding alkenebromonium ions and stability constants of alkene-silver ion π complexes. Subsequent opening of the molecularly bonded π complexes leads, via participation of the nonbonded electron pairs of bromine, to three-membered-ring ethylenebromonium ions (σ complexes). Displacement by bromide ion from the opposite side then accounts for the observed exclusive trans stereospecificity of the bromine addition reactions. Bromine addition to alkynes under similar conditions at 0° also leads to low substrate selectivities indicating a similar concept of electrophilic reactivity of π -donor substrates. Two approaches to structure-reactivity correlations were examined and shown to support the proposed mechanism.

Three-membered ring alkenebromonium ion (σ complex) intermediates have been assumed in the electrophilic addition of bromine to alkenes for many years based on the high stereospecificity of the reactions.¹ Their existence has been confirmed more recently by their preparation and spectroscopic observation (by both σ and π routes) under stable ion conditions.^{2,3}

Other mechanistic paths have also been suggested including charge-transfer complexes (molecular complexes)⁴ or π complexes.⁵ In electrophilic aromatic substitution, kinetic and product distribution data (*i.e.*, consideration of substrate and positional selectivity) have shown that the position of the transition state of highest energy is not fixed but can resemble, depending upon reaction conditions and the nature of the electrophile, either the intermediates (σ complex) or starting materials (π complex).⁶ We have now initiated a study of electrophilic reactions of alkenes and alkynes with electrophiles of varying strength in order to assess the role of π and σ complexes in the reactions. It is hoped that these studies will contribute also to the understanding of the general concept of electrophilic reactivity of unsaturated systems.

The formation of alkene-bromine π complexes has been suggested to explain both the kinetic^{7,8} and spec-

troscopic^{9,10} behavior of these systems. In addition, there has also been reported a low-temperature thermographic study of the propene-bromine system¹¹ in which repeated freeze-thaw cycles were employed to increase the concentration of the complex so that "upon warming a virtually explosive reaction" occurred. Also related is the report⁷ that considerable rate enhancement occurs when bromination is carried out first by cooling an alkene-bromine system (presumably to accumulate the π complex), then allowing the system to warm up rather than carrying out the whole reaction exclusively at the later temperature. While these observations appear to indicate the formation of intermediate bromine complexes, there was no direct evidence available as to either the nature of these complexes or the role they may play in the bromination of alkenes.

Results and Discussion

I. Alkenes. The relative rates of bromination of alkenes in polar solvents, such as methanol, were extensively studied, most notably by Dubois.¹² The data show a close relationship of rate ratios with the electronic effect of alkyl groups, reflecting their effect on the intermediate alkenebromonium ions (σ complexes). We have now determined the relative reactivities of the bromination of a series of representative alkenes in a low-polarity medium, *i.e.*, 1,1,2-trichlorotrifluoroethane (Freon 113) solution. The reactivities compared to ethene were determined by the competitive technique at -35° and are summarized in Table I, along with those of Dubois,¹² for the bromination of the same alkenes in methanol. As a check of the technique we also carried out competitive bromination of permuted alkene pairs, the data of which are included in Table II. In addi-

(1) For reviews see (a) P. B. D. de la Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems," Elsevier, New York, N. Y., 1966, pp 113-149; (b) I. V. Bodrikov and Z. S. Smolyan, *Russ. Chem. Rev.*, **35**, 374 (1966); (c) R. C. Fahey, *Top. Stereochem.*, **3**, 237 (1968).

(2) J. M. Bollinger, J. M. Brinich, and G. A. Olah, *J. Amer. Chem. Soc.*, **92**, 4025 (1970), and previous references cited therein.

(3) G. A. Olah, P. Schilling, P. Westerman and H. C. Lin, *J. Amer. Chem. Soc.*, **96**, 3581 (1974).

(4) D. V. Banthorpe, *Chem. Rev.*, **70**, 295 (1970); this review discusses the difference between these types of complexes.

(5) See G. A. Olah, *J. Amer. Chem. Soc.*, **94**, 808 (1972), for a discussion of π and σ type intermediates.

(6) For a comprehensive review, see G. A. Olah, *Accounts Chem. Res.*, **4**, 240 (1971), and references given therein.

(7) F. R. Mayo and J. J. Katz, *J. Amer. Chem. Soc.*, **69**, 1339 (1947).

(8) C. G. Gebelein and G. D. Frederick, *J. Org. Chem.*, **37**, 2211 (1972).

(9) R. E. Buckles and J. P. Yuk, *J. Amer. Chem. Soc.*, **75**, 5048 (1953).

(10) J. E. Dubois and F. Garnier, *Spectrochim. Acta, Part A*, **23**, 2279 (1967).

(11) V. A. Lishnevskii and G. B. Sergeev, *Kinet. Katal.*, **5**, 407 (1964).

(12) J. E. Dubois and G. Nouvier, *Tetrahedron Lett.*, 1325 (1963).

Table I. Relative Rates of Addition of Bromine to Alkenes Compared to Ethene

Alkene	Br ₂ in CF ₂ ClCFCl ₂ <i>k</i> _{rel} ^a	Br ₂ in CH ₃ OH <i>k</i> _{rel} ^b
Ethene	1.0	1.0
Propene	14	
1-Butene	20	95.7
1-Pentene	12	69.0
1-Hexene	10	65.7
3,3-Dimethylbutene	9	
2-Methylpropene	204	
<i>trans</i> -2-Butene	200	
<i>cis</i> -2-Butene	320	
<i>cis</i> -2-Hexene	460	2890
<i>cis</i> -2-Pentene	881	4160
<i>cis</i> -3-Hexene	846	6435
<i>trans</i> -3-Hexene	676	
<i>cis</i> -3-Methyl-2-pentene	1030	118,800
2-Methyl-2-butene	2300	
2,3-Dimethyl-2-butene	5680	924,000

^a Analyzed by gas chromatography. ^b In CH₃OH + 0.2 *N* NaBr at 25°. Data of Dubois (ref 12).

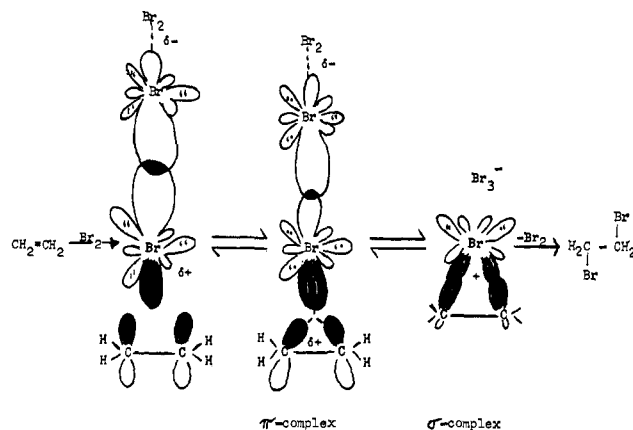
Table II. Relative Rates of Bromine Addition Using Permuted Pairs of Alkenes

Alkene	A/B obsd	C/B obsd	A/C calcd	A/C obsd
A. 1-Butene				
B. 1-Pentene	1.67	.83	2.0	1.17
C. 1-Hexene				
A. 2-Methylpropene				
B. <i>trans</i> -2-Butene	1.02	0.1	10.2	10.1
C. 1-Butene				
A. <i>cis</i> -2-Pentene				
B. <i>cis</i> -2-Hexene	1.94	5.0	0.388	0.383
C. 2-Methyl-2-butene				

tion to illustrate the internal consistency of the data, this also allows for a more accurate determination of values for the more reactive alkenes.

Addition reactions of halogens to alkenes when carried out in low-polarity media are, as is well known, very sensitive to acceleration by light and strikingly catalyzed by small amounts of such polar substances as hydrogen halides and water. Further, the reactions are affected by glass surfaces (the rates can be greatly increased by simply adding glass beads) reflecting the possibility that additions, when performed in the dark, in the absence of polar catalysts, take place predominately on the glass surface of the reaction vessel. Consequently, as surprising as it is, little was known about the nature of halogen additions to alkenes in low-polarity media excluding catalysis by the factors mentioned above. Our work, therefore, has been carried out in Teflon equipment (see Experimental Section) under conditions which exclude the possibility of catalysis by glass, light, moisture, or other external factors.

The reaction of alkenes with bromine in 1,1,2-trichlorotrifluoroethane solution is too fast to measure its rate by noncompetitive methods. However, the competitive method of rate determination overcomes this difficulty, while the data obtained preclude either diffusion or encounter rate-controlled reactions. While in 1,1,2-trichlorotrifluoroethane solution much lower substrate selectivities were observed than in more polar media, the rate differences are still incompatible with limiting encounter rate or diffusion-controlled conditions.

**Figure 1.** The path of addition of bromine to ethene.

Data summarized in Table I indicate that the bromination reactions in the low-polarity solvent system do not reflect a considerable degree of charge development in the transition states, which consequently are considered of the alkene-bromine π complex type. This complex can be envisioned as arising from the initial interaction of the π system of the alkene with the electrophilic bromine, *i.e.*, the polarized bromine molecule *via* interaction with the back lobe of the antibonding orbital of bromine (Figure 1). This interaction would then lead to a three-center bound π complex (alkenonium complex) such as proposed in general for the reaction of electrophiles with alkenes⁵ and postulated for the reaction of the isoelectronic borane with alkenes.^{5,13} It is of particular interest to note that related alkenonium complexes were, indeed, observed under stable ion conditions in the reaction of adamantylideneadamantane with bromine, as well as with other electrophiles, as reported in our accompanying paper.³

Present bromination data indicate that the transition states of the reactions lie early along the reaction coordinate and resemble more the starting alkenes than the intermediate alkenebromonium ions. We suggest that the transition states have the character of oriented, two-electron, three-center bonded alkenonium complexes. This complex, subsequently, *via* cleavage of the bromine-bromine bond as well of the three-center bond and simultaneous participation by the nonbonded electron pairs of the rehybridized bromine atom with the developing carbenium center, forms the three-membered ring bromonium ion intermediate (σ complex) (Figure 1). The latter alkenebromonium ion is then displaced by bromide ion from the accessible backside, accounting for the observed exclusive *trans* stereospecificity of the bromine addition reactions. This is a reaction path similar to that found in electrophilic substitution reactions of benzene and alkylbenzenes with strong electrophiles and is well differentiated from reactions showing "late" transition state character, with the transition state of highest energy resembling alkenebromonium ion intermediates (or σ complexes). If the transition state occurs early along the reaction coordinate, similar to that in electrophilic aromatic substitutions with strong electrophiles, it would be expected that there would be little demand for its stabilization by alkyl substituents and rate differences

(13) P. R. Jones, *J. Org. Chem.*, **37**, 1886 (1972).

would more closely parallel the π -donor ability of the corresponding alkenes, instead of the stability of the related alkylbromonium ions (σ complexes).

A referee suggested that "direct substitution" of the alkene-bromine π complex by bromide ion could also account for the data and thus there is no need to involve the three-membered ring alkylbromonium ions in the suggested mechanism. If this would be the case, however, only a slight effect of substituent alkyl groups on the bromination reactions could be expected, even with increasing alkyl substitution (as in the case of the alkene- Ag^+ complexes). Further, as the intermediacy of cyclic alkylbromonium ions is now well established in electrophilic addition of bromine to olefins, there is no reason to doubt that they are also involved in the reaction path in the present systems.

Though it is difficult to directly compare the stabilities of π and σ complexes of alkenes with reactivities of bromination of the same alkenes, comparisons can be made with available data on silver-alkene π complexes¹⁴ on the one side and the stabilities of the cyclic alkylbromonium ions¹⁵ on the other. Although the stability constants of Ag^+ complexes (summarized in Table III) show some dependence of the numerical

Table III. Heats of Formation of Alkylbromonium Ions^a and Relative Stability of Alkene-Silver π Complexes^b

Ion	ΔH , kcal/mol ^c	π complex	Rel stability const
	+1.0		1.0
	-3.3		0.41
	-11.3		0.18
	-15.5		0.36
	-22.9		0.005

^a Measured at -60° in 11.5 mol % SbF_5 in FSO_3H . Reference 15. ^b Reference 14. ^c Heats of formation of halonium ions (and anions) are from the corresponding vicinal dihalide precursors (in 11.5 mol % SbF_5 in FSO_3 at -60° , kcal/mol). Since the heat of formation of the anion produced is not known, ΔH is a relative quantity. Differences in ΔH represent differences in heats of formation of the ions from the dihalide precursors in solution with the same leaving groups (anions).

values upon a composite of steric, electronic, and solvent effects,^{16,17} the importance of these values lies in the fact that they cover only a very limited range and show only a slight increase in complex stability with increasing alkyl substitution.¹⁶

(14) M. A. Muhs and F. T. Weiss, *J. Amer. Chem. Soc.*, **84**, 4697 (1962).

(15) J. W. Larsen and A. V. Metzner, personal communication and *J. Amer. Chem. Soc.*, **94**, 1614 (1972).

(16) R. J. Cvetanovic, F. J. Duncan, W. E. Falconer, and R. S. Irwin, *J. Amer. Chem. Soc.*, **87**, 1827 (1965).

(17) L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, San Francisco, Calif., 1964, p 88.

In contrast, as shown in Table III based on the data of Larsen,¹⁵ the heats of formation of σ -bonded three-membered ring ethylenebromonium ions, generated from the corresponding vicinal dibromides, show a striking effect of alkyl substitution. Though it is generally accepted that a more stable intermediate ion (carbocation of halonium ion) would be formed faster under kinetic conditions, thermochemical data do not allow a direct conversion of relative stability into relative rates of formation (from an alkene and bromine). However, data of Table III clearly indicate that a very wide range in order of magnitude of relative rates would be expected for a reaction in which the transition state occurs late along the reaction coordinate and thereby resembles in nature the cyclic bromonium ion. This is the case in the work by Dubois¹² and is in contrast to a reaction in which the transition state occurs earlier and thus resembles a π complex (and therefore starting alkenes), such as is indicated in our present work.

While neither the measured bromonium ion nor silver ion complex stabilities are directly comparable with rates of bromination of alkenes,¹⁷ they indicate that the relative rates observed in the present work are much more in accord with a π complex type transition state for the reaction than the σ complex mechanism proposed in polar solvent systems.^{1a} It has been shown for electrophilic aromatic substitutions that a similar change in relative rates is observed in reactions involving either early (π complex type) or late (σ complex type) transition states,⁶ illustrating how relative rate data reflect the nature of the transition states in the reaction.

While previously it was assumed that a π complex type mechanism for alkene additions would result only in negligible spread of relative rate values (corresponding to silver ion-alkene π complex stability constants⁴ or iodine-alkene stability data since both are qualitatively similar),¹⁸ the differences observed in the present work do not seem to support this assumption.¹⁹ Recent theoretical calculations²⁰ are also in accord with this suggestion and indicate that significant differences are to be expected. These calculations on systems involving an alkene and interacting electrophile show that only a weak interaction exists between ethene and silver ion or molecular chlorine but that significant stabilization in the latter case can be obtained by increased chlorine-chlorine bond length and partial charge development. Therefore, it seems likely that since iodine, like silver ion, forms only a weak complex with alkenes, a strict correspondence between measured stability constants and relative rates is not expected. However, because the halogen-halogen bond is not greatly deformed and the alkene and halogen are in close proximity, some correlation as reported here in terms of magnitude or as observed in certain other systems⁸ seems reasonable.

In addition, development of partial charge would allow for the general parallelism between increased alkyl substitution with increased reactivity, as observed

(18) R. J. Cvetanovic, F. J. Duncan, W. E. Falconer, and W. A. Sunder, *J. Amer. Chem. Soc.*, **88**, 1602 (1966).

(19) After our work was originally submitted (in the form of a communication), a report appeared, indicating a correlation of observed relative rates with alkene-iodine stability constant data for three alkenes.⁸ However, there is no justification to claim quantitative behavior of this type to all alkenes based on this limited study.

(20) R. D. Bach and H. F. Henneke, *J. Amer. Chem. Soc.*, **92**, 5589 (1970).

Table IV. Relative Rates of Additions to Cycloalkenes

Reagent	N ^a	Cyclohexene = 1.0		Ref
		Cyclopentene	Norbornene	
Bromine	3	4.2	36	This work
Chromyl chloride	3	4.9	312	b
Ag ⁺	3	2.0	17	14
Diethyl aluminum hydride	4	9.4		c
Ozone	5	3.9	4.3	21
Osmium tetroxide	5	22	72	21
Diimide	6	15.5	450	d

^a The number of atoms, from substrate and reagent, involved in the cyclic transition state of the additions, based on appropriate models. ^b E. W. Garbisch, Jr., S. M. Schilderout, D. B. Patterson, and C. M. Sprecher, *J. Amer. Chem. Soc.*, **87**, 2932 (1965). ^c F. Freeman, P. D. McCart, and N. J. Yamachika, *ibid.*, **92**, 4621 (1970). ^d K. Ziegler, *Justus Liebigs Ann. Chem.*, **589**, 99 (1954).

Table V. Relative Rates of Addition of Bromine to Alkynes

Alkyne	Br ₂ in	Br ₂ in
	CF ₂ ClCCl ₂ F ^a	CH ₃ COOH ^b
3,3-Dimethylbutyne	1.0	1.0
2-Butyne	1.6	
1-Hexyne	2.4	0.61
2-Hexyne	3.0	
3-Hexyne	3.2	33.6

^a For the reaction at 0°, this work. ^b For the reaction at 24.8° relative second-order rate constants, ref 23.

in our study and in other electrophilic reactions of alkenes.

We have also determined the relative reactivities of bromination of cyclohexene, cyclopentene, and norbornene in 1,1,2-trichlorotrifluoroethane solution. The results are listed in Table IV along, for comparison, with some previously reported data of additions to the same cycloalkenes. In the case of the more strained alkenes, higher rates are expected with increasing ring size which should allow for greater relief of strain in the transition state, relative to a smaller size ring.²¹ The data in Table IV do seem to support this hypothesis and relative rate data of the studied brominations indicate that the transition states of the reactions lie early and resemble the starting alkenes.²²

II. Alkynes. For comparison we have also determined the relative rates of bromine addition to some alkyl-substituted alkynes in 1,1,2-trichlorotrifluoroethane solution at 0°. These results are listed in Table V, along with related data obtained by Pincock and Yates for bromination in acetic acid.²³ Temperature effects on the bromination in acetic acid lead to a large negative entropy effect, which was interpreted as due to the involvement of an intermediate alkynebromonium ion. Though the range of rates reported by Pincock and Yates is not very broad, bromination in 1,1,2-trichlorotrifluoroethane does lead to reduced selectivity, similarly as noticed for alkenes. In addition, while alkynes react at rates similar to, or even greater than, the corresponding alkenes in some electrophilic reactions, for these reactions which involve strained bridged (cyclic) transition states, alkynes react up to 10⁵ times

slower than alkenes.²⁴ Similar behavior was also noted in the present study in which alkynes were found to react more slowly by at least a factor of 10⁴ than the corresponding alkenes.²⁵ Though no corresponding π and σ complex stability data are available for alkynes,²⁶ we consider that data summarized in Table V also indicate in the bromination of alkynes a mechanism with an early transition state of π complex nature similar as in the case of the related bromination of alkenes.

The difference in behavior of alkenes and alkynes is quite reasonable when one considers that the decreased reactivity of the alkynes results from an increase in the energy required for initial π complex formation. Since the unsaturated bond in alkynes has cylindrical symmetry along the carbon-carbon bond and involves a measure of electron delocalization,²⁷ total electron availability for complex formation is reduced. This would then require more energy for π complex formation and result in slower rates of reaction.

III. Free-Energy Relationships. The mechanism proposed for the bromine addition reaction reported in this work involves interrelationships between structural effects on observed rates, solvent nucleophilicity, and reagent electrophilicity. In order to provide a better understanding of these factors we have evaluated some other probes into the origins of rate differences in addition reactions to alkenes.

To a first approximation it seems possible to characterize an electrophile in terms of its reactivity with a set of reference bases, such as alkyl-substituted alkenes. A reagent which is highly electrophilic would not discriminate greatly between the members of such a series because of its high reactivity. Conversely, a weak electrophile would tend to show increasing discrimination and result in a relatively higher range of rates. This general type of approach has previously been employed by de la Mare²⁸ who tabulated some values of electrophilic reactions related to rate increases when a methyl group replaces hydrogen in the substrate and by Skell²⁹ who studied the addition of dichlorocarbene to a series of alkenes. Table VI lists the results of the application of this concept to addition reactions employing some typical electrophilic reagents.

The entries in Table VI are obtained from published relative rate data on the reactions of alkenes with chromic acid,³⁰ chromyl chloride,³¹ and chlorine.³² An examination of these entries within each reaction series (*i.e.*, each horizontal row) shows no clear trend of

(24) R. W. Alder, R. Baker, and J. M. Brown, "Mechanism in Organic Chemistry," Wiley-Interscience, New York, N. Y., 1971, p 307.

(25) The observed relative reactivities of an alkene *vs.* the corresponding alkyne were very large but were estimated by the following procedure. To equal amounts of *trans*-3-hexene and 3-hexyne was added (in separate experiments) an equal amount of dilute bromine solution (equivalent to about 0.7% conversion) all at once. No color was detected in the alkene solution after a few seconds (the minimum time possible for such observation), but the color persisted in the alkyne solution for about 3.5 hr. This rough estimate indicates at least a 10⁴ difference in the reactivities.

(26) Some values are listed in ref 13 and referred to in ref 16, but they are too few to show definite trends.

(27) R. T. Morrison and R. N. Boyd, "Organic Chemistry," Allyn and Bacon, Boston, Mass., 1966, p 235 ff.

(28) Reference 1a, p 157.

(29) P. S. Skell and M. C. Cholod, *J. Amer. Chem. Soc.*, **91**, 7131 (1969).

(30) A. K. Awasthy and J. Rocek, *J. Amer. Chem. Soc.*, **91**, 991 (1969).

(31) F. Freeman, P. D. McCart, and N. J. Yamachika, *J. Amer. Chem. Soc.*, **92**, 4621 (1970).





(32) M. L. Poutsma, *J. Amer. Chem. Soc.*, **87**, 4285 (1965).

(21) H. C. Brown and P. J. Geoghegan, Jr., *J. Org. Chem.*, **37**, 1937 (1972).

(22) R. E. Erickson and R. L. Clark, *Tetrahedron Lett.*, 5997 (1969).

(23) J. A. Pincock and K. Yates, *Can. J. Chem.*, **48**, 3332 (1970).

Table VI. Rate Increases with Methyl Substitution

Electrophilic ^a reagent	k_{Me}/k_H				Ref
					
Bromine	14.0	14.3	11.5	2.5	^c
CrO ₄ H ₂		5.8	16.6	5.1	30
CrO ₂ Cl ₂			14.6	19.4	31
Chlorine			220	39.0	32

^a *I.e.*, the precursor to the actual electrophile. ^b Relative rate values, applicable only in comparisons of horizontal rows. ^c This work.

This is generally referred to as an extended Hammett equation. Table VII lists the results obtained for correlation with eq 2 of the present bromination data, as well as those of Dubois in methanol solution, and for comparison some other addition reactions. The *R*, *S*, and *F* values are standard statistical quantities related to the degree of correlation obtained.³⁴ The normalized regression coefficients are "weighted" values which express the relative contributions of each independent variable to the overall equation.³⁵

Equation 2 has previously been employed by a num-

Table VII. Correlation of Data of Addition Reactions with Extended Hammett Equation

Reaction	ρ^*	δ	ρ_n^{*a}	δ_n^a	<i>R</i> ^b	<i>S</i> ^c	<i>F</i> ^d	<i>n</i> ^e	Ref
Bromination in CF ₂ ClCCl ₂ F	-4.43	0.950	-1.94	1.03	0.965	0.303	86.98	16	Present work
Bromination in methanol	-5.53	1.00	-1.86	0.92	0.997	0.132	898.8	12	12
Chlorination	-5.68	0.615	-1.30	0.35	0.971	0.539	40.87	8	32
Oxidation with CrO ₂ Cl ₂	-1.94	-0.180	-0.78	-0.20	0.976	0.319	61.36	9	31
Reduction with diimide	-0.280	0.506	-0.22	1.01	0.790	0.516	2.48	6	^f
Argentation	5.46	1.55	0.49	0.34	0.820	3.24	13.4	16	14

^a Normalized regression coefficients, see text. ^b Multiple correlation coefficient. ^c Standard error of the residual. ^d Maximum calculated *F* level. ^e Number of points correlated. ^f E. W. Garbisch, Jr., S. M. Schilderout, D. B. Patterson, and C. M. Sprecher, *J. Amer. Chem. Soc.*, **87**, 2932 (1965).

the ratio as a function of increasing methyl substitution of the double bond. This is not unexpected in view of the fact that increasing the degree of substitution around the reaction center would introduce variables such as steric and strain effects along with the inductive effect. A more useful representation of the data is seen if the last two columns of Table VI are examined. As shown in both of these columns, the introduction of a methyl group onto *trans*-2-butene or 2-methyl-2-butene produces rate differences which are qualitatively similar. To this approximation it is seen that bromine (as studied in this work) is the strongest electrophile while chlorine is the weakest. The other two reagents are strong electrophiles and of similar nature as would be expected in view of the proposed mechanisms of the oxidations.^{30,31} However, quantitative comparisons cannot be made since it is seen that the magnitude of the effect of methyl group introduction is dependent upon the particular alkene that is chosen as a reference. In addition the ordering of "electrophilicity" of each donor species changes depending upon the reference alkene. There are not sufficient data, as yet, to determine which reference is more appropriate as a measure of electrophilicity. It seems that while this method has potential, its application awaits further clarification of the factors affecting such relative rate data as well as development of another independent method for ordering electrophilic strength in addition reactions.

A more quantitative approach to the problem has been indicated by Taft³³ who correlated rates of ester hydrolysis with a free-energy relationship of the form indicated in eq 1. We have calculated the correlation

$$\log(k/k^0) = \rho^* \sigma^* + \delta E_s \quad (1)$$

of rate data with the indicated summation of Taft's σ^* (polar) and E_s (steric) substituent constants (eq 2).

$$\log k_{rel} = \rho^* \sum \sigma^* + \delta \sum E_s + C \quad (2)$$

(33) R. W. Taft, Jr., in "Steric Effects In Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956.

ber of investigators to correlate addition reactions to alkenes^{12,31} while Charton³⁶ has extensively employed a related equation (using inductive and resonance substituent constants) to correlate many aspects of alkene reactivity.

Excellent results were obtained in the first four reactions, each significant at the 99% confidence level, while poor results were obtained for diimide reduction and argentation. The significant differences obtained for these latter reactions are evidently due to the fact that they are not electrophilic additions as in the first four series. It might be expected that diimide reduction would be subject to factors other than simple inductive or steric effects but the poor correlation of argentation data is not so easily rationalized. Two explanations of this behavior are possible. First, since equilibrium constants are measured, the data analyzed reflect the influence of steric and inductive effects on both the forward and reverse reactions and there is no justification in assuming they are identical. The second explanation arises from the summation procedure of substituent effects which leads to identical values for independent variables though the corresponding alkenes generally react at different rates. Since the alkenes chosen for argentation are also those used in our present bromination study, the argentation data do contain a significant number of isomeric alkenes. This is further supported by eliminating rate values for isomeric alkenes (retaining only *trans* disubstituted alkenes) and then performing the calculation. Using our bromination data, six alkenes were eliminated, and the multiple *R* value increased to 0.981. This is clearly related to removal of alkenes containing specific steric interactions of the substituents with each other.

Though correlations with eq 2 have been calculated

(34) W. J. Youden, "Statistical Methods for Chemists," Wiley, New York, N. Y., 1951.

(35) N. Nie, D. H. Bert, and C. H. Hull, "Statistical Package for the Social Sciences," McGraw-Hill, New York, N. Y., 1970, Chapter 15.

(36) M. Charton and B. I. Charton, *J. Org. Chem.*, **38**, 1631 (1973), and previous papers.

previously, there has appeared no general discussion of the interpretation of the ρ^* and δ values obtained. This is presumably due to lack of consideration of the normalized regression coefficients. Swain and Lupton³⁷ calculated related values in their determination of inductive and resonance contributions to substituent constants used in Hammett correlations of electrophilic aromatic substitution, but extension of their work to alkenes has not previously been attempted.

Since both inductive and steric effects are considered in eq 2, the simple ρ^* or δ coefficient is not sufficient to express the response of the observed rates to these effects. The quantity of interest would be the ratio of the normalized coefficients, R_n , defined as ρ_n^*/δ_n . The discussions presented earlier in this work developed the idea that the bromine addition related to our bromination data was of an early π complex nature and would therefore be less subject to inductive (and possibly steric) effects than a mechanism involving late transition states. The fact that the observed R_n value is 1.88 for our bromination data and increases to 2.02 for those of Dubois supports this hypothesis in a more quantitative manner. While the sensitivity of the regression analysis to structural changes in the transition state is not known, the high quality of the analyses indicates that the ratio changes are significant. The importance of these ratios is further supported by comparison with chlorination data ($R_n = 3.71$) if it is realized that the range of rates reported for each reaction is in the order chlorination > bromination (CH_3OH) > bromination (Freon 113). This increasing sensitivity to inductive effects evidently occurs as the transition state becomes later and resembles a charged cyclic alkylenehalonium ion.

Another point of interest is that while the ρ_n^* values for bromination and chlorination are similar, the δ_n value is significantly smaller for chlorination. Since decreased steric interactions would lead to faster rates of addition all else being equal, this analysis indicates that chlorine addition should occur faster than bromine addition. That this indeed is the case is demonstrated in a recent report of rates of addition of chlorine and bromine to some alkenes and alkynes.³⁸ Without exception, each substrate reacted more rapidly with chlorine than with bromine.

Data of CrO_2Cl_2 oxidation and argentation are difficult to characterize in terms of the R_n value since the sign of the coefficients changes. CrO_2Cl_2 data show negative dependence on E_s while set 6 shows positive dependence on σ^* . This is opposite behavior as seen for halogenation data. Combined with the previous discussion on the poor results obtained for diimide reductions, the data show that interpretation of results obtained for multiple free-energy correlations indicated by eq 2 must include differentiation of the electrophilic (or adding) reagent.

Though there are obvious limitations involved in the application of either of the above mentioned approaches to structure-reactivity correlations, we have demonstrated that both methods support our mechanistic picture of bromine addition to alkenes in 1,1,2-trichlorotrifluoroethane solution. The data presented in Tables

VI and VII show that the initial interaction of electrophilic bromine with an alkene occurs early along the reaction coordinate with consequently reduced charge development and decreased sensitivity to alkyl substitution when compared with related additions. In accordance with the Hammond postulate³⁹ the transition state would resemble starting alkene and is then of three-center, two-electron bound π complex character.

In conclusion it appears to be a general feature of electrophilic reactions of π -donor systems that a diversity of mechanism exists which extends not only to aromatic systems but also to alkenes and alkynes as well. The nature of transition states in electrophilic reactions, either additions (alkenes and alkynes) or substitutions (aromatics), can be varied from one lying early on the reaction coordinate where it would be of π complex type to a late one resembling σ complexes. The former show generally low-substrate selectivity, while they can maintain high-positional (directional) selectivity, whereas the latter are characterized by high selectivity in both regards.

It is apparent that the previously outlined scheme for the reactions of unsaturated systems (alkenes, alkynes, and aromatics) with electrophiles and the concept of the variable nature of transition states, depending on their position along the reaction path (early or late) in these reactions, illustrate a unified concept of electrophilic reactivity for all classes of π -donor substrates.

Experimental Section

Materials. Alkenes used were commercially available materials (Aldrich Chemical or Chemical Samples Co. (liquids), J. T. Baker (gases)) of 99% purity or better and were checked by gas chromatography prior to use. Cyclohexene and cyclopentene (Phillips Petroleum Co.) were distilled before use through a Nester-Faust 24 in. Teflon spinning band column. The alkynes (Farchan Laboratories) were also commercially available and at least 99% pure and were used as received. Bromine (Dow-Ultrapur) was used without further purification. 1,1,2-Trichlorotrifluoroethane (Union Carbide-Ucon Solvent 113-LR1) was dried over MgSO_4 distilled from P_2O_5 and stored over Linde 4A molecular sieve.

Experimental Equipment and Analysis. Temperature control of the bromination experiments was maintained by a Haake Model F constant temperature circulator equipped with a Model K-60 heat exchanger connected to the reaction vessel maintained in an insulated constant temperature bath. Temperature deviation was not greater than $\pm 0.2^\circ$.

Gas chromatographic analysis was performed on a Perkin-Elmer Model F-11 chromatograph equipped with a flame ionization detector, temperature programmer, and flow controller. Peak areas were measured with a Disc integrator. The columns employed were 0.125 in. either 6 or 12 ft 15% SF-96 on 60-80 Chromosorb P, 6 ft 15% DEGS on 60-80 Chromosorb W, or 6 ft 20% SE-30 on 80-100 Chromosorb P. In addition, a 0.125 in. \times 6 ft 20% AgNO_3 (ca. 0.5 M in ethylene glycol) on Chromosorb P was used in conjunction with the previous columns to determine alkene purity.

Proton magnetic resonance spectra were obtained on a Varian Associates Model A56/60 spectrometer; carbon-13 spectra were obtained on a Varian HA-100 spectrometer equipped with a Fourier transform accessory.

Determination of Relative Rates of Bromination. I. Alkenes Vicinal dibromides, required for reference samples, of the C_2 to C_4 alkenes and cyclohexene were commercial materials, purified by distillation. The higher boiling dibromides were prepared on a small scale by direct bromination of the corresponding alkene in 1,1,2-trichlorotrifluoroethane solution. Larger samples were most conveniently prepared by the method of Baird.⁴⁰ All dibromides were checked for purity by gc and nmr.

In order to minimize the variation of observed relative rates

(37) C. G. Swain and E. C. Lupton, Jr., *J. Amer. Chem. Soc.*, **90**, 4328 (1968).

(38) K. Yates, et al., *J. Amer. Chem. Soc.*, **95**, 160 (1973).

(39) G. S. Hammond, *J. Amer. Chem. Soc.*, **77**, 334 (1955).

(40) W. C. Baird, Jr., J. H. Surrige, and M. Buza, *J. Org. Chem.*, **36**, 3324 (1971).

with initial bromine concentration, we chose conditions ensuring minimum bromine concentration. Stock solutions of bromine in 1,1,2-trichlorotrifluoroethane were prepared (about 0.06 *M*) and aliquots taken and diluted to the desired volume. This solution was then added with good stirring over a period of time to a solution of the weighed alkenes, in the same solvent, at the desired temperature. In a typical experiment, 10 ml of stock solution of bromine diluted with 10 ml of additional 1,1,2-trichlorotrifluoroethane was added to the alkene (50 ml of about 0.2 *M* total alkene) at -35° . Since during addition no bromine color was observed, we estimate (based on the rate of bromine addition) a maximum bromine concentration of about 5×10^{-5} *M* at any time. Reactions were run only to a total conversion of about 0.2% so as to attain clear pseudo-first-order conditions. As long as this procedure was followed no effect of relative alkene concentration (fivefold variation in both directions) or per cent conversion (tenfold increase) on the calculated relative rates was observed. The rates listed in Table I were calculated by eq I, where *P* represents

$$k_{\text{rel.1,2}} = (P_1/P_2)/(A_2/A_1) \quad (\text{I})$$

the dibromo product and *A* represents the initial alkene. Reproducibility of the reactions was ensured by using a reaction vessel constructed from Teflon (bored out of a Teflon rod) and closed with a Teflon cap. Reactions were carried out with exclusion of light and surface catalysis by glass; the solutions were stirred magnetically with a Teflon stirring bar. Alkene solutions of known concentration were prepared by direct weighing into precooled solvent or by volumetric techniques. For the light alkenes, mixtures were prepared in a pressure cylinder and passed into cold solvent and the alkene ratios determined by glc. This solution was then used for the competitive brominations. The limitations in the analytical procedure for these alkenes lead to an estimate of 5% accuracy for the values in Table I. All reactions were carried out under dry nitrogen and the Teflon reaction vessel was oven dried and stored in a desiccator between runs. The bromine solution to be added could be cooled by using a jacketed addition funnel incorporated into the cooling system; however, as long as efficient stirring and slow addition was maintained no significant effect was observed when the bromine solutions were not cooled as both runs gave identical results. Relative reactivities of alkenes were generally determined against pentene or *cis*-3-methyl-2-pentene (depending upon observed reactivity) and then expressed as their rate compared to ethene though permuted pairs of alkenes were employed as well (Table II).

For the alkene brominations summarized in Table IV, cycloheptane was used as an internal standard and the relative reactivities were determined by eq II, where *A_i* and *A_f* are the initial and

$$k_{\text{rel.1,2}} = \log (A_{f1}/A_{i1})/(A_{f2}/A_{i2}) \quad (\text{II})$$

final alkene concentration, respectively.

In all cases, under the reaction conditions described above, the vicinal dibromides were the only products found by gas chromatography. This technique was also used to check stereochemistry and kinetic control for the *cis*/*trans* pairs or isomers listed in Table I. In addition, the products from the bromination (separate runs but

identical conditions) of *cis*- and *trans*-2-butene were analyzed by proton⁴¹ and carbon-13⁴² magnetic resonance and shown to give only one product in each case, the diastereomer expected from stereospecific *trans* addition.

II. Alkynes. The required reference dibromoalkenes were most conveniently prepared by the general method of Baird.⁴⁰ Though his method has not been previously applied to alkynes, it does appear to be an excellent technique for the bromination of alkynes. The isolated yields after distillation were 50–70% and gave always 100% *trans*-dibromoalkene as determined by gas chromatography and nmr.²³

All brominations were performed at 0° using the apparatus described above. Due to their low reactivity, the alkynes were reacted in the same manner as alkenes except that the stock solution of bromine used in alkene brominations was diluted tenfold and aliquots of this solution were used. Reactant concentrations similar to the alkenes were determined usually by direct weighing or volumetric procedures. Though slow addition was maintained, some runs showed a faint bromine color upon completion of addition, and these were allowed to stir until decolorized. The observed products were always the *trans*-dibromoalkenes and the relative rates calculated by eq I. In control experiments, small amounts of photochemically isomerized²³ products showed that the *cis* isomer could be detected by gas chromatography.

Calculations

All calculations were performed on a Univac 1108 computer using SPSS, a specifically designed system for statistical analysis.³⁵ A general purpose main program was written for the multiple-regression analysis, mainly to provide proper input and variable transformations. All statistical information, coefficients, and normalized values are provided as output by the system.

In general, the leading reference for each set (Table VII) is the source of the actual rate or equilibrium constants correlated in this work. The values for the independent variable were then calculated using the appropriate substituent constants. The source for each set of substituent constants has been given in the text. Unless specifically mentioned in the text, no rate data were eliminated even if various geometrical isomers were studied.

Acknowledgment. Partial support from the National Science Foundation is gratefully acknowledged.

(41) F. A. L. Anet, *J. Amer. Chem. Soc.*, **84**, 747 (1962).

(42) The ¹³Cmr of the diastereomeric 2,3-dibromobutanes has not been previously reported but is easily rationalized by reference to the reported spectra of the 2,3-dichlorobutanes: C. J. Carman, A. R. Tarpley, and J. M. Goldstein, *J. Amer. Chem. Soc.*, **93**, 2864 (1971), and the population analysis by Anet (ref 40).