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Correlation of Ionization Potentials and HOMO Energies versus Relative Reactivities of Cl_2, of Br_2, and of I_2 with Representative Acyclic Alkenes. Comparison with Other Additions to Alkenes

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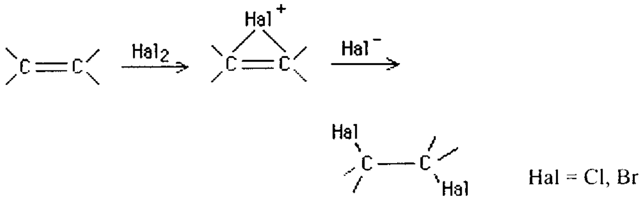
Plots of log k_{rel} versus IP or versus HOMO for the title reactions are presented; similarities and differences among the reactions are discussed. The Cl_2 and Br_2 data each show a single line of correlation with positive slope for all alkenes regardless of the steric requirements; increasing substitution at the double bond increases the reaction rate, indicating an electrophilic reaction. Each plot of the I_2 data calculated for adsorption exhibits a natural separation into groups of similarly substituted alkenes, in which increased substitution reduces the rate. Within each group, a good-to-excellent correlation is observed, with a lower IP generally corresponding to a higher relative rate. The results indicate that the relative magnitude of the steric requirements about the double bond is similar to that of the electronic effects in iodination. Plot shapes for iodination are compared to those of other reactions, such as hydroboration, oxymercuration, complexation with Ag^+, and complexation with $MeHg^+$.

I. Introduction

We have correlated measurable characteristics in addition reactions with alkenes in order to gain information which is useful mechanistically and synthetically. We have applied this technique to several reactions: hydroboration,[1a,b] oxymercuration,[1a,b] bromination,[1a,c] diimide addition,[1d] oxidation with permanganate,[1e] epoxidation,[1f] sulfenyl halide addition,[1f] mercuric chloride complexation,[1f] silver ion complexation,[1c,f] carbene addition,[1g] nitrosyl chloride addition,[1g] oxidation with osmium tetroxide,[1g] and the Wacker oxidation.[1h] The technique can often (1) determine relative magnitudes of steric and electronic effects in the rate-determining step; (2) predict, in a simple way, the effects of substituents on reaction rates for synthetic purposes; and (3) select between alternative proposed reaction mechanisms, in some cases. The previous investigations[1] applied this simple method by correlating the logarithms of the relative reaction rates (log k_{rel} values) with the alkene ionization potentials (IPs) and with their highest occupied molecular orbital energies (HOMOs); reactions with similar mechanisms gave correlation plots which were similar in appearance. To develop further this new technique and to elucidate synthetically and mechanistically important information from experimental or computational data, we apply the technique to important reactions with a variety of mechanisms.

Independent rate studies of chlorination,[3] bromination,[4] and iodination[5] of alkenes allow examination and comparison of steric and electronic effects caused by increasing the degree of substitution at the doubly bonded carbons of acyclic alkenes. In bromination, such steric effects are smaller than electronic effects since one line of correlation is obtained which includes all alkenes, regardless of the degree of substitution at the double bond.[1a,4] For chlorination, in nonpolar media and free from radical contributions,[3] relative rates parallel those of bromine addition, and the plot obtained is similar, as expected (eq 1).



Studies of alkene iodination explored the adsorption (A ⇌ B) of the olefin with solid iodine on a GC column to give the charge-transfer complex B, and complexation (B

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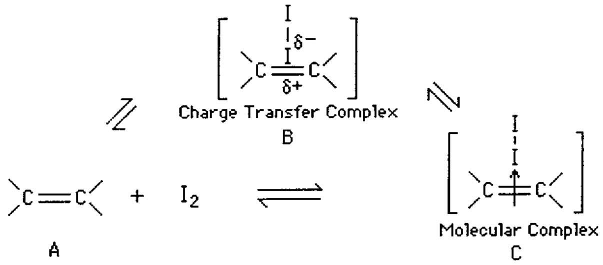
⇌ C) from the adsorbed alkene B to give the molecular complex C.[5]



Comparing the relative steric and electronic effects of these reactions would increase their synthetic utility.

We previously contrasted the bromination of alkenes against hydroboration,[1a] oxymercuration,[1a] and a number of other reactions of alkenes involving three-membered intermediates or products.[1b,c] We determined that hydroboration and oxymercuration each had multiple lines in the plots, grouping alkenes with steric effects which were of the same order of magnitude.[1a] However, bromination gave one line for all alkenes, indicating that the steric effects in that reaction were of the same order of magnitude for all of the alkenes studied, similar to what was observed for the other reactions involving three-membered intermediates.[1b,d] To explore the effectiveness of this procedure and increase the synthetic utility of the reaction, it seemed desirable to determine if these results for bromination are also applicable to the reactions of alkenes with chlorine and iodine; we report the results of that comparison herein.

II. Background

The general procedure[1] for gathering information about the relative magnitudes of steric versus electronic effects in the transition state of the rate-determining step, and therefore about the mechanistic pathway, is the following: (1) relative rates of reaction (k_{rel} values) of a number of representative alkenes, with a broad range of electronic and steric properties are determined; (2) ionization potentials (IPs), highest occupied molecular orbital energies (HOMOs), and in some cases, lowest unoccupied molecular orbital energies (LUMOs) are obtained, because these are relatively insensitive to steric effects; (3) log k_{rel} values of the alkenes are plotted against the alkene π IPs, HOMOs, or LUMOs; (4) plots and correlation coefficients are examined for linearity and number of lines, with each line representing a group of alkenes having steric effects with similar orders of magnitude in that reaction; and (5) plot shapes are compared with those from other reactions in order to ascertain similarities.

In our previous investigations of addition reactions of representative acyclic alkenes,[1] a plot of IPs or HOMO energies versus the logarithm of relative rates shows a natural grouping of data points corresponding to the number of alkyl groups attached to the double bond. Data for the groups of more highly substituted alkenes fall together in the portion of the plot corresponding to lower relative rates of reaction. The rate retardation for more highly substituted alkenes must be due to the rate-retarding steric effects over-riding the rate-increasing, electron-donating electronic effects of the alkyl groups.

In contrast, other addition reactions of acyclic alkenes give only one line in such plots, regardless of the degree of substitution. In these, the reaction rates are of the same order of magnitude regardless of the degree of substitution about the double bond.[1] In these cases, the overall effect of increasing the degree of substitution is rate-increasing, which means that electronic effects override the steric effects.

III. Results and Discussion

Table 1 lists k_{rel} values of representative acyclic alkenes with chlorine,[3] bromine,[4] and iodine.[5] It also lists alkene IPs and HOMOs. In designated cases, IPs were not available and had to be determined through comparison with HOMOs, which were calculated as described previously.[1a] Plots of alkene IPs or HOMOs versus log k_{rel} values are shown in Figures 1−4. Since a higher IP value corresponds to electron removal from a lower-energy molecular orbital, IPs were listed with increasing magnitude proceeding down each plot, in order to make the plots comparable to those using HOMO energy levels.

A. Bromination. Although we did not include so many large substituents on the alkenes in our previous alkene bromination study,[1a] we have included them in this study. Each of the plots of alkene IP and HOMO versus log k_{rel} for bromination[4a−g] ($Br_2/NaBr/MeOH$), shown in Figure 1, has one line of correlation with $r = 0.97$. In both plots, this correlation is better than those found within groups of sterically similar alkenes. In a study reported by Dubois and Mouvier,[4c] it was necessary to utilize a two-parameter equation, employing Taft's inductive σ^* constant and steric substituent constant, to achieve a linear correlation because of the steric requirements of the substituents. In the study reported herein, which includes alkenes with large substituents, a linear correlation with the IPs was again obtained; this means that this type of study may be more likely to give a suitable treatment without use of additional steric parameters.

Similar correlations and plots (not shown) of IP versus log k_{rel} values for bromine addition under other conditions[3a] ($Br_2/HBr/CH_2Cl_2$) gave one line of correlation regardless of the number of alkyl groups on C═C and with an excellent correlation coefficient ($r = 0.98$). Data and plots (not shown) for bromine addition in the presence of HOAc[3b] showed virtually no correlation for all alkenes ($r = 0.26$) or for sterically similar groups; it is unlikely that this is due to the acidic conditions, since bromination[3a] using Br_2/HBr gave good results. Rather, it is probably the case that each alkene included in the study using HOAc[3b] had a functional group which could offer conju-

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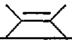
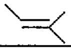
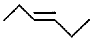
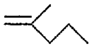
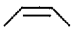
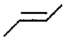
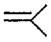
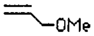
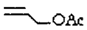
Table 1. Alkene IPs, HOMOs, and Relative Reactivities for Reactions with Chlorine, Bromine, and Iodine

				Relative reactivity					
no.	alkene	IP[a] (eV)	HOMO energy level	Cl_2[b]	Br_2[c]	I_2[d]			
						with support		without support	
						adsorp	complex	adsorp	complex
1		8.27	-9.49	4.3×10^7	1.40×10^6	7.3	3.6	34	16.4
2		8.68	-9.63	1.1×10^6	1.40×10^5	3.5	4.5	9.6	11.9
3		8.95	-9.76		9.76×10^3	31[e]	32[e]	35[e]	33[e]
4		8.97	-9.76		3.57×10^3	4.4[e]	4.3[e]	6.6[e]	6.4[e]
5		9.08	-9.79	1.6×10^4[f]	895	11.0	4.8	18	7.8
6		9.12	-9.79	6.3×10^3	4.05×10^3	7.9	23	9.6	28
7		9.12	-9.77	5.0×10^3	2.62×10^3	1.73	5.0	2.5	7.2
8		9.24	-9.78	5.8×10^3		1.26	5.2	2.5	10
9		9.44[g]	-10.17		7.20				
10		9.45	-9.96	115	40.48	34[h]	43[h]	34[h]	44[h]
11		9.48	-9.97		100	100[i]	100[i]	100[i]	100[i]
12		9.63	-9.94		148	41	118	40	117
13		9.74	-9.97	100		7.1	73	7.7	78
14		9.93[j]	-10.49	5×10^{-5}					
15		10.09[k]	-10.34		0.72				
16		10.18[l]	-10.53		0.7				
17		10.34[l]	-10.48	0.30	0.06				

[a] All IPs, including those in footnotes, are first IPs from ref 2, unless otherwise noted. [b] Reference 3a. [c] Reference 4a–g. [d] Reference 5. [e] Data for the corresponding 2-pentenes; IP's = 9.04 eV (cis) and 9.04 eV (trans). [f] Data for 2-methyl-1-butene; IP = 9.15 eV. [g] Reference 6. [h] Data for 3-methyl-1-butene; IP = 9.52 eV. [i] Data for 1-pentene; IP = 9.48 eV. [j] Reference 7. [k] Reference 8. [l] Reference 9.

gative stabilization directly to an alkenyl carbon and could thereby stabilize a carbocation formed from the alkene; this could lead to the involvement of mixed reaction mechanism pathways.

Last, we should note that this treatment does not consider the effect of the simultaneous reaction of Br_3^- with alkenes. Although the rate of reaction of Br_3^- is slower than that of Br_2, the difference in rate is not sufficient to justify disregarding it.[4i,j] However, comparisons of these reactions have shown not only that substituents affect the two reactions similarly and only in differing magnitudes,[4j,k] but also that the effects of the substituents are roughly parallel.[4k] The fact that the results obtained for chlorination are similar to those obtained for bromination, as will be seen below, also supports the conclusion that the effects must be roughly parallel, since the formation of Cl_3^- is unimportant in that system.[4l]

B. Chlorination. The plots (Figure 2) for chlorination ($Cl_2(g)/O_2$/dark[3a]) each show that the best correlation is obtained by considering all alkenes as a single group with the correlation coefficients $r = 0.99$ (IP) and 0.95 (HOMO). This result is very similar to that for bromination. The reactivities of the alkenes in this reaction are interpreted[3a,c] as compatible with a transition state, which involves partial bonding of the chlorine molecule with both termini of the olefinic system, and with little development of positive charge on one carbon, as in a π complex. This transition state is preferred to one which involves attack at a single terminus with development of carbocation character on one carbon; this conclusion is also very similar to that for bromination.

Because the chlorination study[3a] included only one compound with a large substituent, the authors found it necessary to use only the σ^* constant in order to achieve linear correlation. However, attempts to include allyl chloride in that correlation gave less satisfactory results. In contrast, allylic compounds and alkenes with large substituents were included in our previous study and are included in the correlations reported herein, both without problems.

As in the previous chlorination study, the position of the alkyl substituent on the double bond has little effect on the rate; there is little difference among the chlorination or bromination data for isobutene, *cis*-2-butene, and *trans*-2-butene, but there is a large difference between the chlorination and bromination data for both methylpropene and 2-methylbutene.

Poutsma warned of dangers in extrapolating from linear to branched alkenes since branching stabilizes possible carbocation formation, this could switch the mode of chloronium ion decomposition or switch the mechanism from one with a cyclic chloronium intermediate to one with an open carbocation. While we found no problems achieving correlation with the branched olefins studied herein, we do find problems including aryl

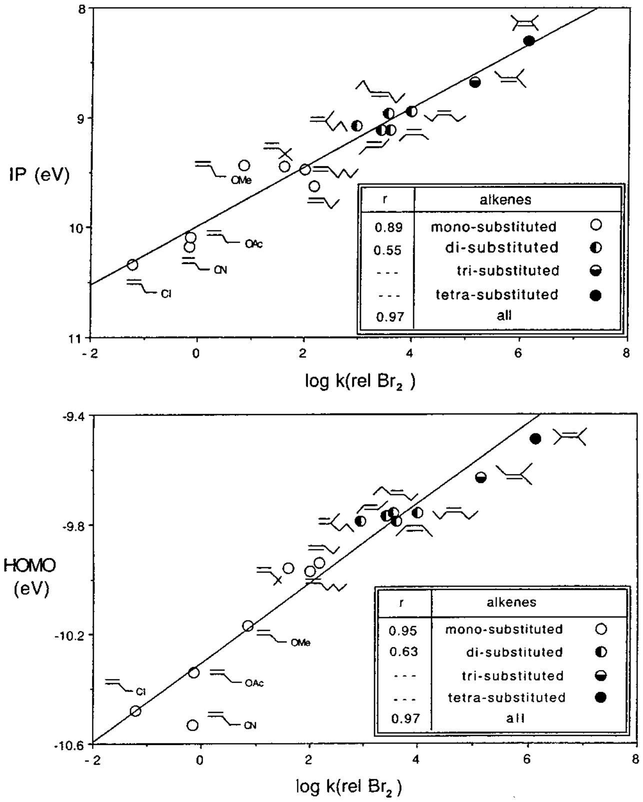


Figure 1. (a) Plot of log k_{rel} Br_2 versus IP for reaction conditions Br_2 /NaBr/MeOH; ref 4a–g. (b) Plot of log k_{rel} Br_2 versus HOMO for reaction conditions Br_2/NaBr/MeOH; ref 4a–g.

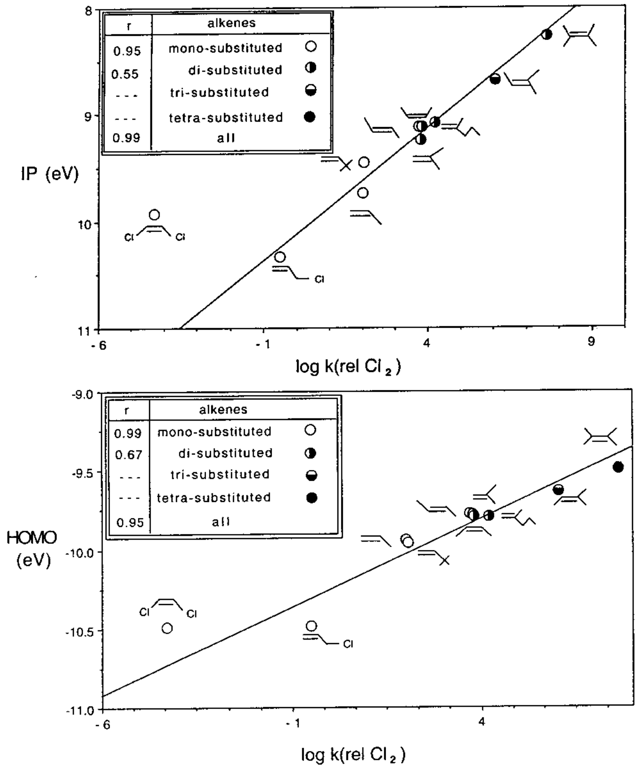


Figure 2. (a) Plot of log k_{rel} Cl_2 versus IP for reaction conditions $Cl_2(g)/O_2$/dark; ref 3a. (b) Plot of log k_{rel} Cl_2 versus HOMO for reaction conditions $Cl_2(g)/O_2$/dark; ref 3a.

substituents, probably for that reason. Although data for dichloroethene were not included in Poutsma's correlation,[3] we attempted to include it here and found that its point fell far off the correlation line (Figure 2). It is possible that the chlorine substitution directly on the double bond converts the reaction mechanism in a manner similar to one of the mechanistic pathway changes discussed above.

Chlorination data, obtained using Cl_2/HOAc,[3b] were plotted versus IPs[7,11] (or HOMO, values in parentheses). As with the results obtained for bromination in the study using HOAc, we found no correlation for sterically similar groups, $r = 0.83$ (0.16) and $r = 0.43$ (0.41), or for all alkenes, $r = 0.14$ (0.36) (plots not shown). Once again, the alkenes included in this study[3b] each had a functional group which could offer conjugative stabilization with a carbocation and could lead to involvement of mixed reaction mechanism pathways.[3d]

C. Iodination. Results for iodination[5] (by using I_2 on GC column support material) are different from those for bromination and chlorination. Studies of the interaction of olefins with molecular iodine were carried out by using a gas chromatographic technique. These explored the complexation equilibria of the olefin interacting with solid iodine on the column: an equilibrium corresponding to adsorption of the gaseous alkene molecules on solid iodine ($A \rightleftharpoons B$), and an equilibrium between the adsorbed alkene and the complexed alkene ($B \rightleftharpoons C$). Each equilibrium was treated mathematically in two ways, accounting for complexation with untreated support and not accounting for it. For adsorption ($A \rightleftharpoons B$), regardless of consideration for untreated support interaction, the data points group depending upon the steric requirements of the alkenes (Figure 3a,b), giving multiple lines with a positive slope. In the plots for these equilibria, a much better correlation is obtained by using separate lines for monosubstituted alkenes ($r = 0.78$ when considering interaction with untreated support and $r = 0.79$ when not considering it) and for disubstituted alkenes ($r = 0.73$ considering interaction with untreated support and $r = 0.70$ not considering interaction) than by considering all alkenes as one group ($r = 0.36$ considering interaction with untreated support and $r = 0.06$ not considering interaction).

For the second equilibrium (between the adsorbed alkene and the complexed alkene, $B \rightleftharpoons C$), regardless of consideration for untreated support interaction, a better correlation is shown in Figure 3c,d with one line of negative slope containing data for all alkenes, irrespective of their steric requirements ($r = 0.76$ considering interaction with untreated support and $r = 0.62$ not considering interaction). The negative slope in each of the plots in Figure 3c,d indicates that the product has an increased amount of electron density in the π bond. One explanation for this phenomenon, which has been

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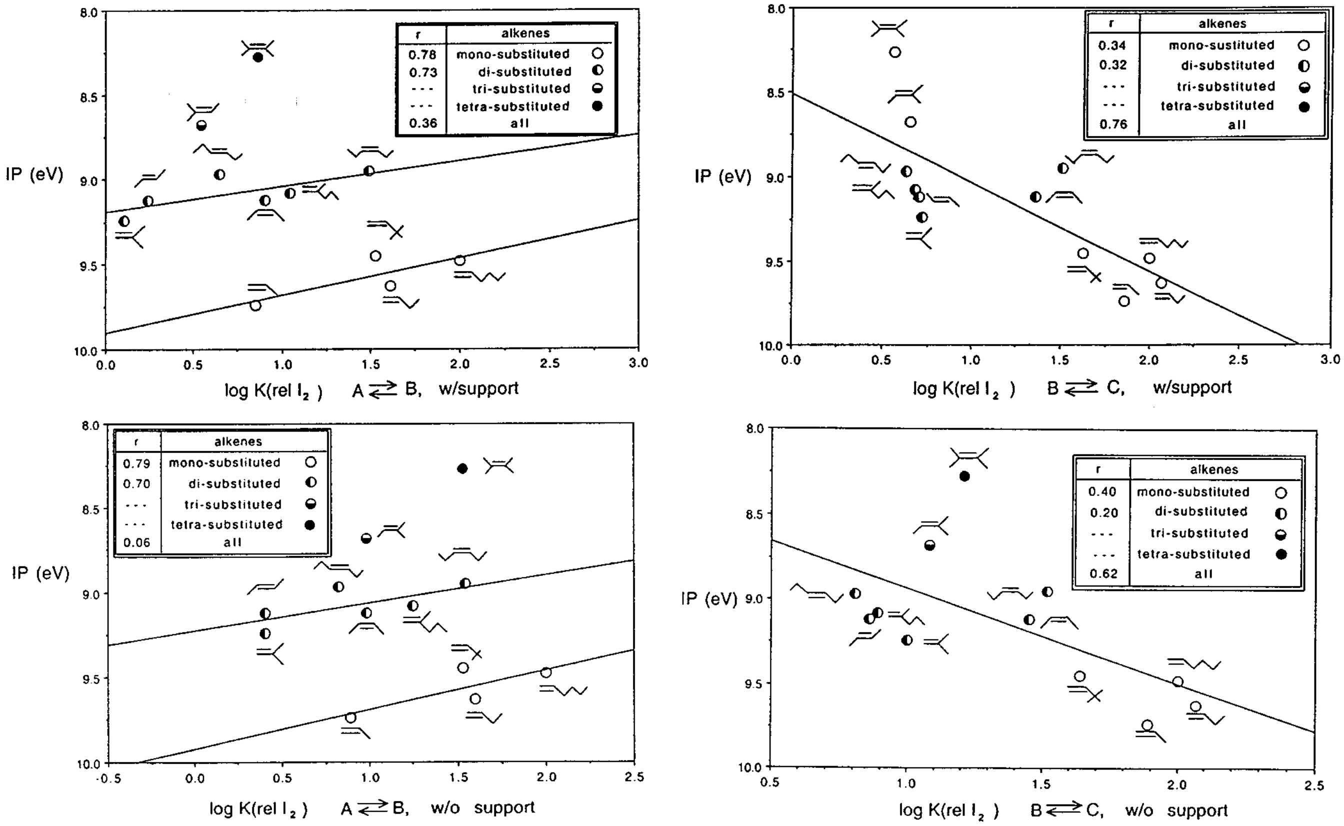

Figure 3. (a) Plot of log K_{rel} I_2 versus IP for adsorption (A $\rightleftharpoons$ B) of I_2 on GC column support material; ref 5. (b) Plot of log K_{rel} I_2 versus IP for adsorption (A $\rightleftharpoons$ B) of I_2 on GC column support material, interaction with support mathematically removed; ref 5. (c) Plot of log K_{rel} I_2 versus IP for complexation (B $\rightleftharpoons$ C) of I_2 on GC column support material; ref 5. (d) Plot of log K_{rel} I_2 versus IP for complexation (B $\rightleftharpoons$ C) of I_2 on GC column support material, interaction with support mathematically removed; ref 5.

proposed in other systems,[5,10b,12] is that back-bonding from the electrophile (here I_2) to the alkene could be absent in the adsorbed form B and present in the complex C.

Electrophilic character in the adsorption step (A $\rightleftharpoons$ B), and nucleophilic character in the complexation from adsorption (B $\rightleftharpoons$ C), reveal information regarding the direction and character of electron transfer in these steps. One explanation for these data, which agrees with eq 2, is that electron density is transferred from the alkene to iodine in the adsorption step (A $\rightleftharpoons$ B), and there is a net increase in the amount of electron density in the π bond in going from the adsorbed alkene to the complexed one (B $\rightleftharpoons$ C). Perhaps the transfer of electron density from iodine to the alkene via back-bonding is more important in the complexed form than in the adsorbed form.

The manifestation of grouping according to alkene steric requirements for adsorption (Figure 3a,b), but not for complexation starting from the adsorbed alkene (Figure 3c,d), might seem surprising because adsorption should be a "looser" interaction, with the molecules farther apart and reduced steric effects. However, because complexation is from the adsorbed alkene, perhaps there would be little additional congestion incurred in this transformation so no grouping according to steric requirements would appear in the plots.

Different results for iodination as opposed to those for chlorination and bromination might seem surprising at first, but they are easily explained. Bromination and chlorination are addition reactions which go to completion. The reaction with iodine does not go to completion because it is unfavorable entropically and is endothermic; it is a reversible complexation reaction in which the equilibrium favors the reactants. Therefore, the plot obtained from reaction with iodine might be expected to resemble those of other alkene complexations instead of those of bromination and chlorination.

D. Comparison to Complexation with Metal Ions or with Organometals. Comparison of the plots for iodination versus those for complexation with the silver ion ($AgNO_3$)[1f,5,10a] reveals similarity (Figure 4a,b). Correlation of log K_{rel} I_2 versus alkene IP gives different results depending upon the equilibrium which is being considered. The plot for A $\rightleftharpoons$ B shows groups of data which form multiple lines, having a positive slope and corresponding to alkenes with different steric requirements; that for B $\rightleftharpoons$ C shows one line with a negative slope, independent of alkene steric requirements. Correlation of log K_{rel} Ag^+ versus alkene IP can also give a different plot appearance, depending upon the experimental method used to obtain the equilibrium constant data. Like the results for the reaction with I_2, these are multiple lines with a positive slope or one line with a negative slope.

As we reported[1f] earlier, if Ag^+ complexation data are obtained by allowing the alkene to become distributed between two liquid phases, then the plot (shown in ref 1f) has multiple lines, each with a positive slope and corresponding to a group of sterically similar alkenes.

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(12) Bach, R. D.; Weibel, A. T.; Patane, J.; Kevan, L. *J. Am. Chem. Soc.* **1976**, *98*, 6237.

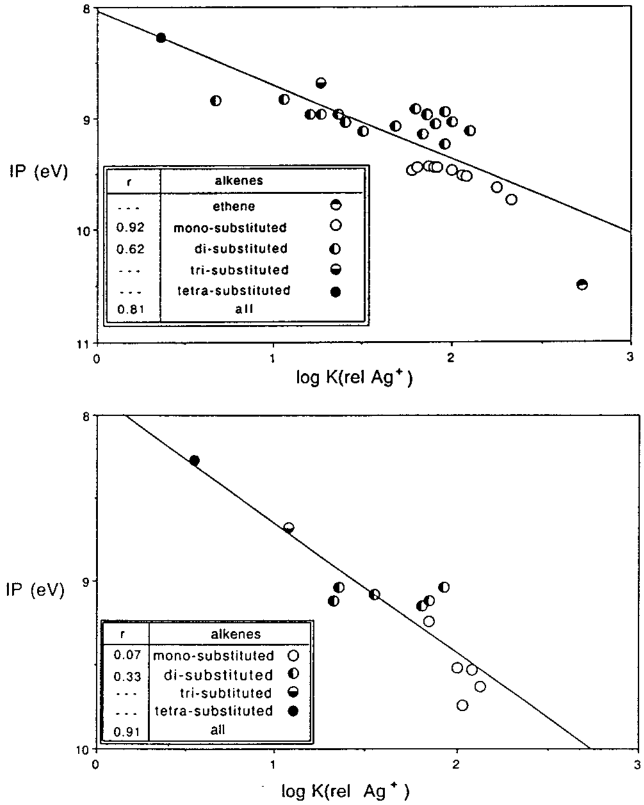

Figure 4. (a) Plot of log K_{rel} Ag^+ versus IP for adsorption (A $\rightleftharpoons$ B) of Ag^+ on GC column support material; ref 10a. (b) Plot of log K_{rel} Ag^+ versus IP for adsorption (A $\rightleftharpoons$ B) of Ag^+ on GC column support material; refs 5, 10.

That plot pertains to the complexation equilibrium[10a] (A $\rightleftharpoons$ C) between the free alkene plus Ag^+ and the complexed alkene. However, it appears to be similar to that for the adsorption of the alkene on iodine (A $\rightleftharpoons$ B) shown in Figure 3a,b. This similarity in plots is apparent although the equilibria being examined are not reported to be the same. There are at least two possible explanations for this. (1) The overall complexation of alkene with Ag^+ in solution proceeds via the adsorbed form (i.e., A $\rightleftharpoons$ B $\rightleftharpoons$ C) but reflects the steric requirements of the reactant alkenes. (2) Formation of the product is by direct complexation from the free alkene A $\rightleftharpoons$ C, which accommodates (and reflects) the steric requirements of the alkene.

Plots for alkene adsorption (A $\rightleftharpoons$ B) with iodine (Figure 3a,b) and silver ion[1f] are somewhat similar to the plots obtained for oxymercuration and hydroboration of alkenes,[1a] except for the placement of data for 1,1-disubstituted alkenes and trisubstituted alkenes. In the adsorptions, 1,1-disubstituted alkenes are in a "disubstituted alkenes" group with 1,2-disubstituted alkenes, and trisubstituted alkenes are separate; in oxymercuration and hydroboration, 1,1-disubstituted alkenes are in a "terminal alkenes" group with 1-hexene, and 1,2-disubstituted alkenes are in an "internal alkenes" group with the trisubstituted alkenes. It is interesting that these plots would be so similar even though the former two are equilibria reactions and the latter two are kinetically controlled reactions.

Equilibrium data for silver ion complexation which correspond to B $\rightleftharpoons$ C are determined by GC.[5,10a] Plots of log K_{rel} vs IP or HOMO give one line of correlation with a negative slope (Figure 4a,b), regardless of the steric requirements of the alkenes ($r = 0.81$[10a] and $r = 0.91$,[5] respectively). Plotted data from either study of the equilibrium, between the alkene adsorbed on Ag^+ and the alkene complexed with Ag^+ (B $\rightleftharpoons$ C), is similar to the analogous plots for iodination (also B $\rightleftharpoons$ C). As in the case of the iodination adsorption to complexation equilibrium (B $\rightleftharpoons$ C), the negative slope indicates the product has an increased amount of electron density in the π bond. Cvetanović[5] made note of the similarity between I_2 complexation and Ag^+ complexation (both give plots with one line of negative slope, B $\rightleftharpoons$ C), as well as of the nucleophilic character of the Ag^+ complexation. He attributed[10b] the latter to a back-donation of electrons to the olefin from the silver ion; this is similar to our discussion for iodination above.

Bach[12] also noted a similarity between the results of calculations for alkenes complexed with methylmercury cation and those with silver ion. He explained that "the bonding in silver and mercury π complexes is due largely to overlap of the filled π orbital of the alkene with the vacant s orbital of the metal. The amount of $d\pi - p\pi$ back bonding of metal electron density with the antibonding π orbital of the alkene is minimal."[12] He also cited differences between the effect of increasing alkyl substitution on the alkene in the data for the reactions of alkenes with methylmercury cation (rate increasing in gas phase by ion cyclotron resonance) and in those for complexation with silver ion (rate decreasing in solution). These gas phase (ICR) data do not collect in sterically similar groups, which is in contrast with the behavior of the oxymercuration data (multiple lines, positive slopes),[1a] which leads to comparable intermediates in solution. The appearance of the plot (not shown, single line, positive slope, $r = 0.85$) obtained from the gas phase (ICR) data[12] for complexation with $MeHg^+$ is also at odds with those from the gas phase (GC) data for complexation with Ag^+ (B $\rightleftharpoons$ C, single line, negative slope)[5,10a] or with I_2 (adsorption A $\rightleftharpoons$ B, multiple lines, positive slope, Figure 3a,b; complexation B $\rightleftharpoons$ C, single line, negative slope, Figure 3c,d).[5] This indicates that the intermediate and/or the mechanism involved in the reaction with $MeHg^+$ is not the same as that in the reaction with Ag^+ or I_2.

E. Summary of Patterns in Plot Appearance and Reactions. The following patterns appear in the above reactions. (1) Chlorination and bromination are similar in that the rate-determining step is the formation of the halonium ion, and the plot of IP versus log k_{rel} yields one line with a positive slope regardless of the steric requirements of the alkenes. The plots indicate that the rate-determining step in each is an electrophilic addition influenced more by electronic effects than by steric effects. (2) Adsorption with iodine (A $\rightleftharpoons$ B) and complexation with silver ion in solution (A $\rightleftharpoons$ C) are similar because plots of IP versus log k_{rel} give lines of correlation with positive slope and with data grouped according to the degree of alkene substitution: monosubstituted, disubstituted, and trisubstituted. (3) Upon including in the mathematical treatment of the data an equation which relates the equilibrium constant of adsorption of gaseous alkene molecules on solid iodine to the equilibrium constant of complexation with solid iodine of alkene molecules physically adsorbed on solid iodine, the appearance of the plots for iodination switches from multiple lines with positive slope to one line with negative slope. (4) Equilibria (B $\rightleftharpoons$ C) for complexation from the adsorbed form in the reaction of alkenes with I_2 or Ag^+ cause the best correlation line in each plot of IP versus log k_{rel} to be one line with negative slope, which includes data for all alkenes regardless of steric requirements. (5) Switching the phase of reaction with Ag^+ or mercuronium ion generation from solution to gas phase causes the correlation lines in the IP versus log K_{rel} plots to switch from multiple lines of positive slope to one line of positive slope. (6) Little back-bonding has been predicted in complexes with Ag^+ or HgX^+, and back-bonding is not possible in hydroboration. However, back-bonding in complexes of alkenes with Ag^+ or I_2 would explain the change in slope in going from adsorption (positive, electrophilic) to complexation (negative, nucleophilic). It is not clear that those conclusions can necessarily be used to predict the significance of back-bonding in complexation with other metal ions or molecules. (7) Oxymercuration and hydroboration give results similar to those in (2) except that the data are grouped according to whether there is an unsubstituted end of the double bond, terminal vs internal instead of monosubstituted vs disubstituted.

IV. Conclusion

Chlorination and bromination give plots of alkene IP versus log k_{rel} which are characteristic of typical electrophilic additions to alkenes. Iodination gives plots which are dependent upon the treatment of the data to reflect adsorption or complexation of the alkene on solid I_2. Adsorption of the alkene on iodine results in grouping according to alkene steric requirements in the plots of alkene IP versus log K_{rel}, whereas complexation from the adsorbed alkene shows no such grouping. Data for reactions of alkenes with I_2 and with Ag^+ appear to be similar to each other, but different than those for reactions that give mercuronium ions; this may be due to changing reaction conditions.

Reactions considered herein, with similar mechanisms and steric and electronic requirements in the rate-determining step, give plots similar in appearance. Therefore, it follows that it should be possible to use correlations and plots such as the ones in this report to gather information about and/or to distinguish between reaction mechanisms and intermediates which are under consideration for a given reaction. One example is to differentiate in iodination between adsorption ($A \rightleftharpoons B$), which has no back-bonding and gives multiple lines with positive slope in the plot, versus complexation from the adsorbed form ($B \rightleftharpoons C$), which is predicted to have a small, but significant, amount of back-bonding and gives a single line of negative slope in the plot. Another example is to differentiate between a kinetically controlled reaction in which electronic effects have a greater influence than steric effects, such as bromination, which has a single line of positive slope in the plot, versus adsorption ($A \rightleftharpoons B$) or complexation ($B \rightleftharpoons C$) of iodine, which have plots as described in the previous sentence. Examples of the use of this technique to differentiate between a reaction involving a three-center intermediate I or product P with the rate-determining step leading to I or P (giving a plot with one line of positive slope) versus one with the rate-determining step leading from I or P (giving a plot with multiple lines of positive slope) have been reported.[1]

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