The Use of Relative Magnitudes of Steric Effects to Explore Reactions of Molecular Halogens With Representative Acyclic Alkenes

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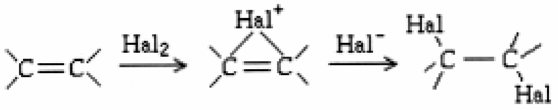
In some addition reactions of acyclic alkenes, plots of ionization potential (IP) versus the log of relative rate show a natural grouping of data points corresponding to the number of alkyl groups attached to the alkene carbons. Plots corresponding to the reaction of Cl_2, Br_2, and I_2 with representative alkenes are presented; similarities and differences among the reactions are discussed. A plot of the I_2 data exhibits a natural separation into groups of similarly-substituted alkenes, in which increased substitution reduces the rate. Within the groups of similarly-substituted alkenes, a good-to-excellent correlation is observed, with a lower IP generally corresponding to a higher relative rate. The Cl_2 data and Br_2 data each show a similar correlation but without separation into similarly-substituted groups. Increasing substitution increases the reaction rate where Cl_2 or Br_2 is employed, in contrast to cases in which I_2 is employed. *©2000 Oklahoma Academy of Science*

INTRODUCTION

We have developed a simple procedure for ascertaining whether additions to acyclic alkenes exhibit steric effects which are either dependent on the degree of substitution about the double bond, or are of the same order of magnitude regardless of the degree of substitution about the double bond (*1-5*). Such information improves the understanding of the reaction and its synthetic usefulness. In this procedure, (a) relative rates of reaction of a number of representative alkenes, with a broad range of electronic and steric properties are determined; (b) log k_{rel} (log of the relative rate compared to that of the reference alkene) of each alkene is plotted against the alkene þ ionization potential (IP); and (c) 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. Alkene IPs are used for comparison because they are relatively insensitive to steric effects.

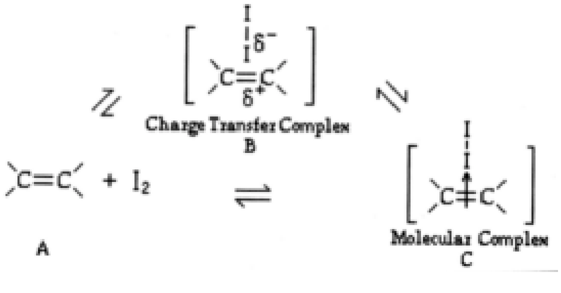
We previously contrasted bromination of alkenes against hydroboration and oxymercuration (*1*) and compared it to a number of reactions of alkenes involving 3-membered intermediates (*2*). We determined that hydroboration and oxymercuration each have multiple lines in the plots, indicating they each have groups of alkenes with steric effects which are of the same order of magnitude within groups, but different from one group to another (*1*). However, bromination gives one line for all alkenes, indicating that steric effects in that reaction are of the same order of magnitude for those alkenes studied, similarly to most of the other reactions involving three-membered intermediates (*2*). In order to explore the effectiveness of the procedure, it seemed desirable to compare bromination to the reactions of alkenes with chlorine and with iodine; therefore, we report the results of that comparison.

For chlorination, in nonpolar media and free from radical contributions (*7*), relative rates parallel those of bromine addition.



Hal = Cl, Br

Studies of alkene iodination explored adsorption (A $\rightleftharpoons$ B) of the olefin with solid iodine on a GC column to give a charge-transfer complex B and complexation (B $\rightleftharpoons$ C) from the adsorbed alkene B to give the molecular complex C (*12*).



RESULTS and DISCUSSION

Table 1 lists relative rates of reaction (k_{rel}) of representative acyclic alkenes with chlorine (*7*), with bromine (*8-11*), and with iodine (*12*) and also lists alkene IPs and highest occupied molecular orbital (HOMO) energy levels. Relative reactivities in the table are relative to each other, with 1-hexene selected as the reference and given the value of 100. In some cases, IPs were not available and had to be determined through comparison with HOMOs, which were calculated as described previously (*2*). Plots of alkene IPs versus log k_{rel} values are shown in Figures. 1-3. Since a higher IP corresponds to electron removal from a lower-energy molecular orbital, IPs were plotted in inverse order on the y-axis of each plot, in order to make the plots comparable to those using HOMO energy levels. These plots reveal results for chlorination (one line of correlation with the correlation coefficient, $r = 0.99$) which are very similar to those for bromination (one line of correlation with $r = 0.97$).

Results for iodination (*12*) are more complicated. Studies were carried out in order to observe the interaction of olefins with molecular iodine by using a gas chromatographic (GC) technique. The results were analyzed in order to explore both absorption and complexation of the olefin with iodine on the column. Each set of data was further treated mathematically in two ways: (a) accounting for complexation with untreated support and (b) not accounting for complexation with untreated support.

The plots for reaction with iodine are unlike those for chlorination and for bromination. In treatments that allowed complexation with the support, adsorption and complexation with iodine gave conflicting results. Adsorption showed a grouping according to the amount of steric hindrance, whereas complexation shows no such grouping. However, the level of correlation in these plots is only moderate.

When complexation with support was not allowed, again adsorption showed the grouping and complexation does not (Figures 3a-d). The level of correlation in these plots is much higher, especially for adsorption, which has a correlation coefficient of 0.8 and 0.7 for mono- and di-substituted alkenes, respectively. The manifestation of grouping for adsorption, but not for complexation, is surprising, because adsorption should be a much “looser” interaction with the molecules farther apart.

At first the different results might seem surprising, but they are easily understood. 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. Although the iodonium ion is presumably formed, the equilibrium favors the reactants. Therefore, the plot obtained from reaction with iodine might be expected to resemble that of alkene complexation with silver ion ($AgNO_3$) (*2*). Comparison of the two plots does indeed reveal an obvious similarity. Each plot has multiple lines, with positive slopes and good-to-excellent correlations, and groups the alkenes according to their steric requirements.

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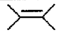
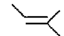
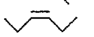
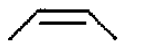
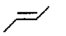
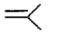
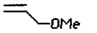
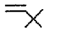
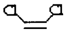
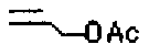
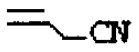
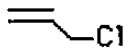
TABLE 1. Alkene IP's, HOMOs, and relative reactivities for reaction with chlorine, with bromine, with iodine.

no.	alkene	IP[a] (eV)	HOMO energy level	relative reactivity					
				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	1.40×10^3	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[i]	100	100[j]	100[j]	100[j]	100[j]
12		9.63	-9.94		148	41	118	40	117
13		9.74	-9.97			7.1	73	7.7	78
14		9.93[k]	-10.49	5×10^{-5}					
15		10.09[l]	-10.34		0.72				
16		10.18[m]	-10.53		0.7				
17		10.34[m]	-10.48	0.30	0.06				

[a] All IPs, including those in footnotes, are 1st IPs from ref 2, unless otherwise noted.

[b] Ref 3a.

[c] Ref 4a-g.

[d] Ref 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] Ref 6.

[h] Data for 3-methyl-1-butene; IP = 9.52 eV.

[i] Data for 1-pentene; IP = 9.48 eV.

[j] Ref 7.

[k] Ref 8.

[l] Ref 9.

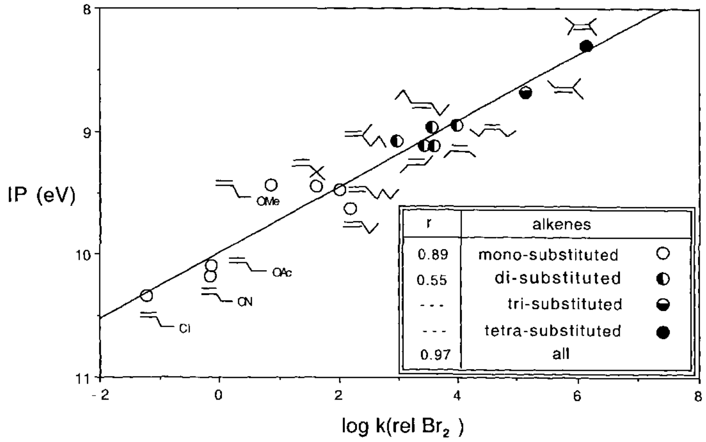


Figure 1. Plot of log k_{rel} Br_2 versus IP for reaction conditions Br_2 /NaBr /MeOH (*8-11*).

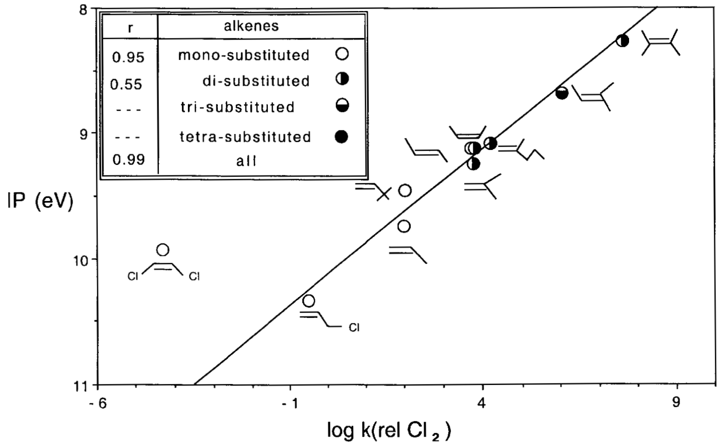


Figure 2. Plot of log k_{rel} Cl_2 versus IP for reaction conditions Cl_2 gas /O2 / dark (*7*).

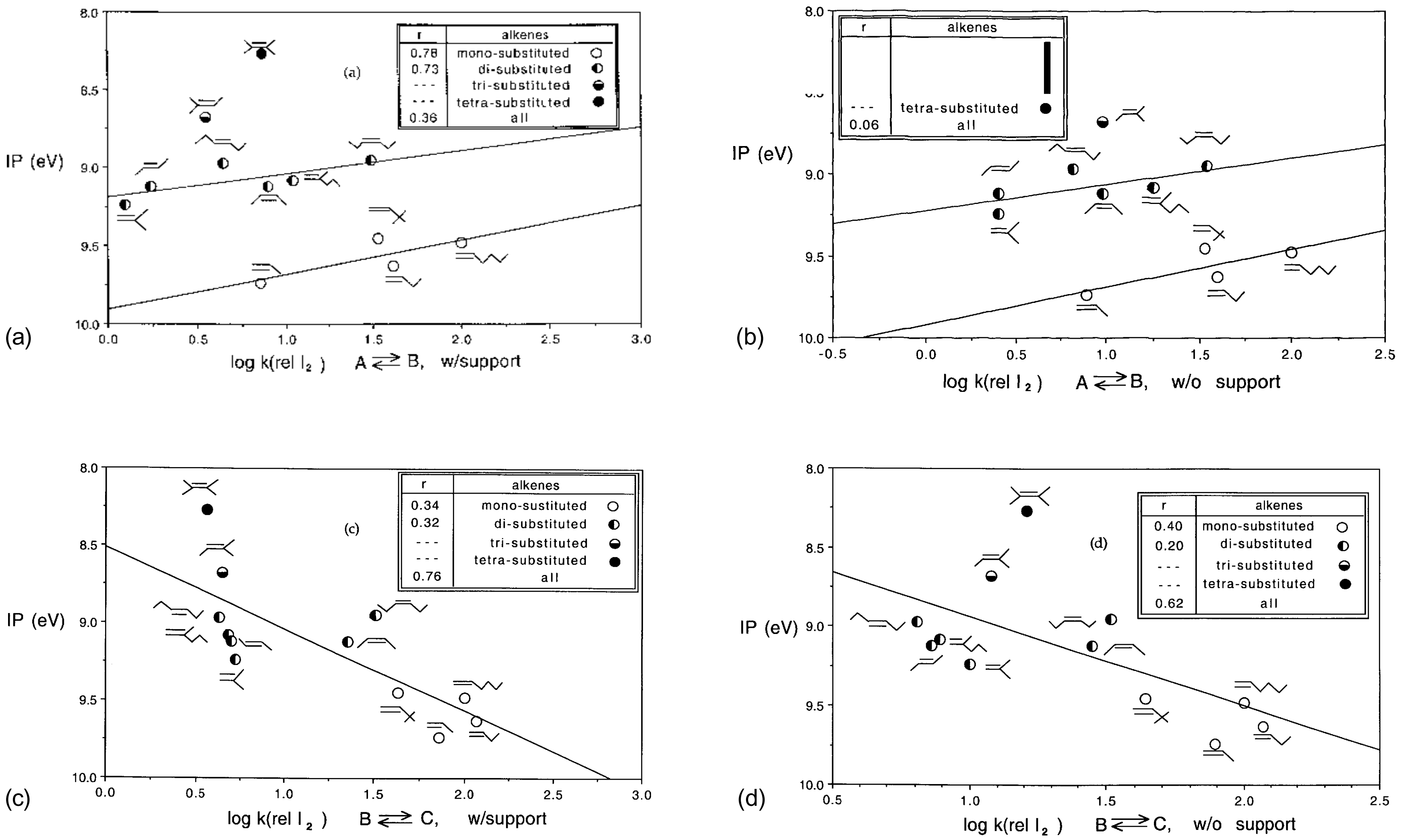


Figure 3. Plots of log K_{rel} I_2 versus IP using data subjected to various mathematical treatments: (a) Adsorption (A $\rightleftharpoons$ B) of I_2 on GC column support material, (b) Adsorption (A $\rightleftharpoons$ B) of I_2 on GC column support material; interaction with support mathematically removed. (c) Complexation (B $\rightleftharpoons$ C) of I_2 on GC column support material. (d) Complexation (B $\rightleftharpoons$ C) of I_2 on GC column support material; interaction with support mathematically removed (*12*).

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