

## DIIMIDE REDUCTION OF REPRESENTATIVE ALKENES AND CORRELATION OF THEIR RELATIVE REACTION RATES WITH CORRESPONDING IONIZATION POTENTIALS

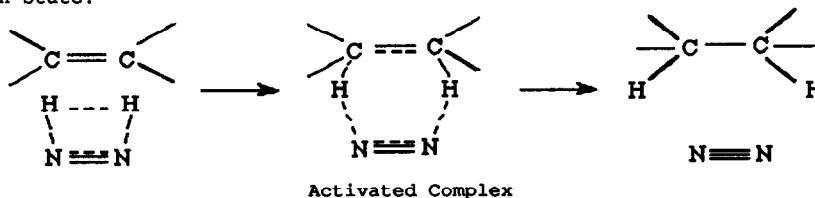
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**Abstract:** The plot of the log of relative rates of diimide reduction of representative alkenes versus their ionization potentials (IP's) exhibits a natural separation into sterically similar groups, indicating the importance of steric effects. Within each group, a good correlation is observed with a lower IP corresponding to a higher relative rate, demonstrating electronic effects in sterically similar molecules.

### Introduction

We have investigated various addition reactions by correlating the logs of relative rates of reaction of representative alkenes with their IP's.<sup>2</sup> We have shown that reactions with similar rate-determining transition state structures give similar correlation plots. The plots are similar in that they have similar slopes and numbers of lines which reflect like steric requirements and electronic effects. Within each group, a good correlation is observed with a lower IP corresponding to a higher relative reaction rate. We have demonstrated the use of such correlations to differentiate between reactions in which the intermediate is a three-membered ring preceded by the rate-determining step versus (1) those in which a three-membered ring intermediate is followed by the rate-determining step<sup>2d</sup> and (2) those which are equilibria with three-membered rings as products.<sup>2a</sup> We now extend our studies to diimide reduction of alkenes,<sup>3-7</sup> which proceeds through a six-membered cyclic transition state.<sup>4,5</sup>



This reaction has been widely used in organic synthesis due to its special selectivity toward multiple bonds.<sup>3</sup> It is a useful alternative to, and in some cases is advantageous over, catalytic hydrogenation.<sup>4</sup> The carbon-carbon double bond is generally reduced readily by diimide, while multiple polar bonds such as those in the functional groups nitro, sulfoxyl, and cyano are left intact under the same reaction conditions.<sup>4</sup> Substitution on the double bond plays an important role; the rate of diimide reduction decreases rapidly as the number of substituents on the double bond increases.<sup>4</sup> This was analyzed<sup>8</sup> as indicating that electron donating substituents decreased the rate of reaction. However, since a variety of substituents was not used previously, a proper treatment of steric and electronic effects in the reaction was impossible.

### Results and Discussion

The experimental results of diimide reduction of some selected alkenes are summarized

Table I. Relative rate constants for diimide reduction of alkenes and their IP's

No.	Alkene	Product(s) and approx. yields	$k_{rel}$	IP (eV) <sup>g</sup>
1		100%	272.	-8.48 <sup>a</sup>
2		100%	138.	-9.44
3		100%	120.	-9.67 <sup>c</sup>
4		100%	105.	-10.09
5		100%	100.	-9.48
6		100%	71.4	-9.85 <sup>d</sup>
7		100%	67.2	-9.00 <sup>f</sup>
8		100%	36.6	-10.39 <sup>g</sup>
9		100%	16.5	-9.04 <sup>b</sup>
10		100%	13.9	-9.08
11		100%	13.4	-9.04 <sup>b</sup>
12		100%	8.89	-9.70 <sup>e</sup>
13		100%	4.74	-8.68
14		100%	3.76	-10.00
15		100%	2.31	-8.30
16		50% , < 5%		-10.34
17		5-10% , < 10%		-10.18
18		0% , < 10%		-9.75 <sup>i</sup>
19		0% , < 10% CH <sub>3</sub> CH <sub>3</sub>		-9.85
20		0% , < 10% CH <sub>3</sub> CH <sub>3</sub>		-9.82
21		0% , < 10% CH <sub>3</sub> CH <sub>3</sub>		-10.91 <sup>h</sup>
22		0% , < 10% CH <sub>3</sub> CH <sub>3</sub>		-9.73 <sup>h</sup>
23		0% , < 10% CH <sub>3</sub> CH <sub>3</sub>		-10.79 <sup>h</sup>
24		0% , < 10% CH <sub>3</sub> CH <sub>3</sub>		-10.10 <sup>h</sup>

<sup>a-h</sup>Superscripts refer to ref. 9. <sup>i</sup>Second IP.

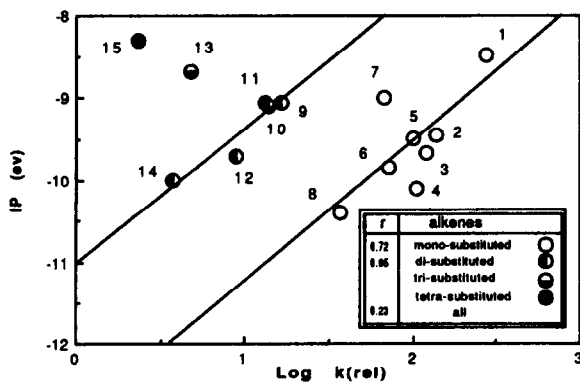


Figure 1. Correlation of the relative rates for diimide reduction of alkenes with their IP's. Numbers next to data points refer to alkenes in Table I.

in Table I. The diimide reduction procedures,<sup>7</sup> analyses,<sup>2</sup> and competitive reactions<sup>2</sup> were carried out as described earlier. Reactivities are reported relative to 1-hexene. Reduction yields, based on GC analyses, refer to yields of alkanes from their corresponding alkenes.

We found that some functionalized alkenes (allylic halides and some vinylic compounds) do not give the desired product, the functionalized alkane, upon reaction with diimide. Instead, a small amount of the corresponding parent alkane and several other compounds in smaller quantities are observed. (See Table I, entries 16-24.) Products were identified by GC coinjection with an authentic sample and by GC/MS. Thus, we could not include these alkenes in our study. Nevertheless, it is interesting that diimide apparently can reduce not only  $\pi$ -bonds, but also some  $\sigma$ -bonds. We subjected propyl chloride, propyl bromide, and propyl iodide to the same reaction conditions<sup>7</sup> used for the corresponding allylic halides above and obtained the same simple alkanes, which supports the idea of  $\sigma$ -bond reduction.

Figure 1 shows the correlation between the logs of relative rate constants for diimide reduction of alkenes and their first IP's. The alkenes fall into sterically similar groups according to the degree of substitution. The correlation<sup>10</sup> is good for monosubstituted alkenes (correlation coefficient  $r = 0.72$ ) and excellent for disubstituted alkenes ( $r = 0.95$ ). Within each group, as the IP increases (with electron-donating substituents), the rate of reduction increases. The regressed lines for the mono- and disubstituted alkenes have roughly the same slope (1.70 for monosubstituted alkenes and 1.65 for disubstituted alkenes).

Since IP's of alkenes are directly related to the electronic effects of the substituents on the double bond, the slope of the regressed lines in Figure 1 reflects the degree of dependence of the relative rates on the electronic effects. A larger slope would correspond to a smaller dependence of relative rates on electronic effects. The similar slopes of the regressed lines indicate that electronic effects are approximately the same for monosubstituted and disubstituted alkenes. The degree of separation between regressed lines indicates a significant dependence of relative rates on steric effects. A steric effect in the transition state has been cited as one reason why trans alkenes have higher reactivities than cis alkenes.<sup>4</sup> On the basis of the above facts and analysis, Figure 1 shows that the relative rates of diimide reduction of alkenes are dependent on both steric effects and electronic effects.

The correlation shown in Figure 1 indicates that diimide reduction is controlled by the frontier molecular orbitals of the alkenes and diimide. This is because the first IP's of alkenes represent their HOMO energy levels and generally correspond to the  $\pi$  energy levels.<sup>2d</sup> MNDO calculations for the compounds listed in Table I were carried out as described earlier<sup>2</sup> in order to insure that the  $\pi$  electrons of each alkene occupy the HOMO. The second IP is given for the one case in this study in which the  $\pi$  electrons occupy the NHMO. (See Table I.) Generally, the correlation between the IP and  $k_{rel}$  also is the correlation between the HOMO and  $k_{rel}$ .<sup>2</sup> Therefore, the rates of reaction of alkenes toward diimide reduction increase in direct proportion to their  $\pi$ -electron energy levels.

The results of our correlation differ sharply in several ways from those reported earlier.<sup>8</sup> (1) The reactivities of alkenes toward reduction are dependent upon electronic effects; electron-donating groups increase the rate of reaction. The previous report indicated that electron-donating groups decrease the rate of reaction. (2) The steric effect is significant; the higher the degree of substitution at the double bond, the slower the alkene is reduced. The previous report did not indicate a steric effect due to increased substitution on the double bond. (3) While attempting to include a variety of

functionalized alkenes, we found that allylic halides and some vinylic compounds can be reduced only partially, if at all, to their corresponding alkane products. The previous report was not so concerned with including a variety of functionalities.

The plot of diimide reduction of alkenes is very similar to that for hydroboration of alkenes.<sup>2</sup> This shows that both reactions are controlled by both electronic and steric effects. However, the separation between the two regressed lines for hydroboration is much larger than that for diimide reduction. This means that the steric effects for hydroboration are much more significant than those for diimide reduction. In contrast, the plot for diimide reduction is different from bromination of alkenes, which has only one line and no significant steric effects.<sup>2</sup>

However, some other additions involving a cyclic transition state, such as chromyl chloride oxidation of alkenes<sup>11</sup> and iodine isocyanate addition<sup>12</sup> show different characteristics. In the latter reactions, (1) a higher degree of substitution at the double bond corresponds to a higher reaction rate, (2) cis alkenes show a higher reactivity than trans alkenes, and (3) the reaction rate is highly sensitive to electronic effects. The reasons for the different characteristics are the subject of further studies.

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