The Reaction of Diimide with Olefins in the Gas Phase[1]

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Abstract: The gas-phase hydrogenation of olefins by diimide has been studied at 100°. It is suggested that the reaction involves synchronous transfer of two hydrogen atoms from *cis*-diimide and that the overall rate is controlled by the isomerization of *trans*-diimide to form the reactive cis isomer. The first-order rate constant for this isomerization at 100° was found to be 1×10^{-2} sec^{-1}. Relative rates of reaction of *cis*-diimide with a number of olefins were estimated to be as follows: ethylene (1.0), *trans*-butene-2 (0.33), *cis*-butene-2 (0.11), 1,3-butadiene (0.065), cyclohexadiene (~0.05), 2,3-dimethylbutene-2 (~0.02). It was also estimated that the rate of reaction of *cis*-diimide with *trans*-diimide to yield N_2H_4 and N_2 was between 4 and 8 times faster than its reaction with ethylene. The mechanism and nature of the reaction are discussed.

Diimide, N_2H_2, generated *in situ* has been extensively used in the liquid phase as a reagent for the stereospecific hydrogenation of unsaturated molecules.[4] In recent work in this laboratory we have studied some of the properties of N_2H_2 in the gas phase and found it to decompose in a rather complex manner, yielding N_2, H_2, and N_2H_4, with a half-life of several minutes at room temperature.[5] The reaction with several olefins was examined briefly, and while they suppressed the formation of H_2 at very low diimide concentrations, the yield of hydrogenation products was extremely low. This was in agreement with an earlier observation of Mock, who reported no hydrogenation when gaseous diimide was passed into a solution of azobenzene or olefins at room temperature.[6]

The present paper describes a more detailed study of the reactions of diimide with olefins in the gas phase, chiefly at 100°, at which temperature we have found the hydrogenation reaction to be much more efficient.

Experimental Section

Diimide was prepared together with an excess of ammonia by passing anhydrous hydrazine (Matheson Coleman and Bell) vapor through a weak microwave discharge as described previously.[5] The N_2H_2–NH_3 mixture, roughly 1:10, was collected in a U trap at liquid nitrogen temperature and rapidly vaporized into the reaction vessel by warming with hot water.

Ethylene, *cis*- and *trans*-butene-2, and 1,3-butadiene (Matheson of Canada, Research Grade) were used without purification other than the removal of noncondensible gases. 2,3-Dimethylbutene-2 (Aldrich Chemical) was thoroughly outgassed. The sample of 1,3-cyclohexadiene obtained from Aldrich Chemical was contaminated with its disproportionation products, benzene and cyclohexene; it was purified by gas chromatography and stored at Dry Ice temperature to minimize further disproportionation.

Diimide concentration was measured by its absorption at 345 nm, taking a value of 4 for the decadic molar extinction coefficient. Our previous value[5] of 6 (±3) leads to yields of reduction products greater than 100% at high olefin pressures. There was considerable uncertainty in that estimate,[5] and since the absorption spectrum of diimide is sharply banded,[7] the value may also depend somewhat on the bandpass of the spectrophotometer; the value of 4 was chosen to give limiting yields of alkanes of about 100% and is thus an upper limit.

Hydrazine concentration was measured by its absorption at 240 nm, using a decadic molar extinction coefficient[5] of 53. Hydrocarbon products of the diimide–olefin reactions were analyzed by gas chromatography. No attempt was made to determine yields of N_2 or H_2 in the present experiments.

The cylindrical quartz reaction vessel (10 cm long, 2.5 cm diameter), fitted with Suprasil optical windows obtained from Hellma (Canada) Ltd., was mounted in a heated compartment in the light beam of a Heath spectrophotometer. Usually, diimide was vaporized rapidly into the cell and the olefin added quickly, within a few seconds; in a few experiments olefin was introduced first. Measure-

ment of the initial composition of the reaction mixture was based on direct estimation of N_2H_2 by its absorption at 345 nm and measurements of olefin pressure, making corrections for the lack of mixing in the filling line (60 cm of 0.2 cm i.d. tubing). After reaction was complete the condensible gases in the cell were trapped in a U tube at −196° and transferred by distillation to a glass sample tube (~5 cm^3 volume) which was subsequently broken in the gas chromatograph inlet system to inject the sample. The flame ionization detector was fairly inert to the large volume of ammonia always present from the diimide preparation, but the overall sample size had to be limited to avoid peak distortion.

The initial diimide concentration and its decay during the reaction was normally monitored by the spectrophotometer; in a few experiments hydrazine formation was followed instead.

Results

Preliminary experiments with several olefins confirmed that there was little reaction with diimide at room temperature, with yields of reduction products amounting to only a few per cent of the diimide initially present. At 100°, however, the reactions were much more efficient, apparently approaching, within the uncertainty of the estimate of diimide concentration, a quantitative reaction of diimide at high pressures of the more reactive olefins. This is shown in Figure 1 where the fraction of N_2H_2 reacted to form reduction product is plotted against the olefin:diimide ratio, for several olefins.

Olefin pressures ranged from about 3 to 360 Torr in these experiments, and the initial N_2H_2 pressure ranged from about 4 to 17 Torr. Within the experimental scatter the fraction of the diimide reacting with each olefin depends only on the olefin:diimide ratio, with no systematic dependence on the absolute diimide pressure. Each olefin gave a unique reduction product with diimide, corresponding in the mono-olefins to simple addition of hydrogen to the double bond. Reaction with 1,3-butadiene gave almost exclusively[8] 1-butene, while 1,3-cyclohexadiene gave cyclohexene.

Although olefins react efficiently with diimide at 100°, surprisingly they *reduce* rather than increase the rate of disappearance of diimide. Figure 2 shows a composite first-order plot of the decay of diimide combining data from a number of separate experiments; it is seen that diimide decays initially with a rate constant of about 2×10^{-2} sec^{-1}. Figure 3 shows the effect of added olefin on this initial rate of decay, reducing it to about half its value at a high pressure of olefin.

Olefins also strongly suppress the formation of hydrazine in the system. Figure 4 shows the formation of hydrazine from diimide decomposition in two separate experiments done under very similar conditions of diimide concentration and total pressure. In one experiment 100 Torr of ethylene was added and in the other 100 Torr of nitrogen. The ob-
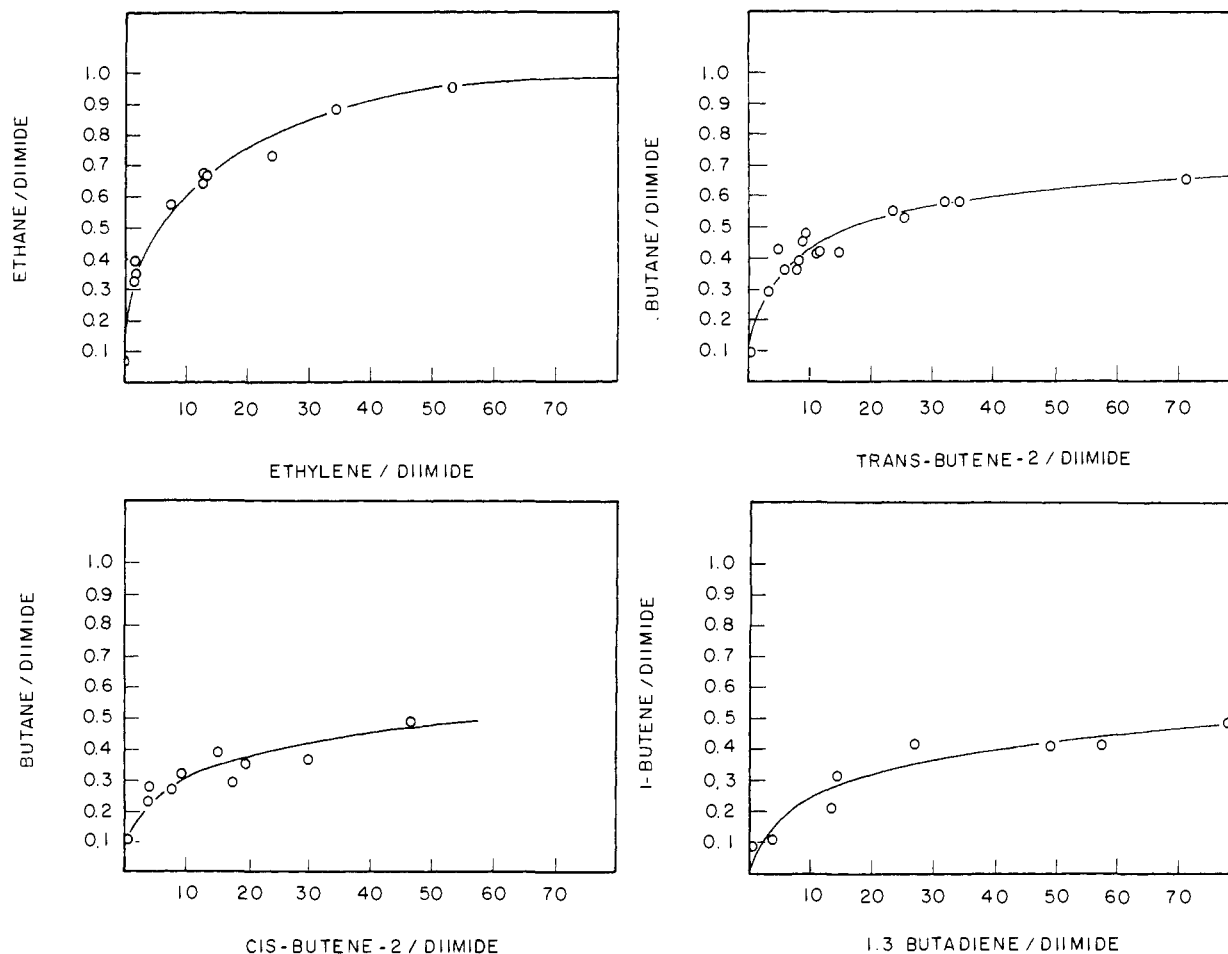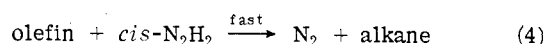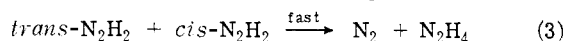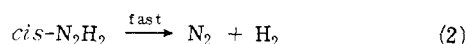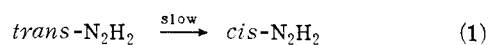
Figure 1. Yields of reduction products from the reaction of diimide with four olefins, expressed as a fraction of the diimide initially present, and plotted against the initial ratio of olefin to diimide.

served reduction in hydrazine formation was approximately equal to half the ethane produced. Other experiments at various pressures of olefin confirmed this behavior.

Discussion

In the gas phase at 100°, diimide hydrogenates olefins with reasonable efficiency, and the data in Figure 1 suggest a simple competition between reaction with olefin and the normal decay processes. The reaction with olefins, however, results in a *reduced* rate of diimide disappearance, and this somewhat bizarre kinetic behavior points to an unusual reaction mechanism. The following scheme fulfills the requirements.

$$trans\text{-}N_2H_2 \xrightarrow{\text{slow}} cis\text{-}N_2H_2 \tag{1}$$

$$cis\text{-}N_2H_2 \xrightarrow{\text{fast}} N_2 + H_2 \tag{2}$$

$$trans\text{-}N_2H_2 + cis\text{-}N_2H_2 \xrightarrow{\text{fast}} N_2 + N_2H_4 \tag{3}$$

$$\text{olefin} + cis\text{-}N_2H_2 \xrightarrow{\text{fast}} N_2 + \text{alkane} \tag{4}$$

It is envisaged that reaction 1 is slow and rate controlling, while reactions 2, 3, and 4 are fast and competitive. In the absence of olefins, it was observed that at very low concentrations of diimide, reaction 2 was predominant, and N_2 and H_2 were produced in equal amounts.[5] As the concentration of diimide was increased, the yield of H_2 decreased toward zero while N_2 and N_2H_4 were formed by reaction 3. In the presence of olefins, reaction 4 competes with 2 and 3, and the yields of both H_2 and hydrazine are suppressed.

An essential feature of the mechanism is the slow, rate-controlling formation of a reactive form of diimide. There is

no direct evidence that the cis isomer is the transient reactive species, but it appears to be the most likely possibility. *trans*-Diimide is known to be the predominant form in the gas phase,[5,7] and in fact *cis*-diimide has only been tentatively identified in a low-temperature matrix.[9] Participation of an unstable cis isomer has been suggested before[5,6] in the decomposition of diimide, and certainly the most reasonable structures for the transition states of reactions 2, 3, and 4 require a cis conformation. The only serious objection to reaction 1 is that reasonable estimates of the barrier to isomerization suggest that the rate would be too slow;[10] there is, however, no prior experimental information whatsoever about the process.

From the proposed mechanism, assuming a steady state in *cis*-diimide, the rate of disappearance of *trans*-diimide (T) is given by

$$d[T]/dt = -k_1[T]\left(1 + \frac{k_3[T]}{k_2 + k_3[T] + k_4[\text{olefin}]}\right) \tag{5}$$

In the absence of olefin, two limiting cases are clear. At high diimide concentrations, reaction 1 is always followed by reaction 3, i.e., $k_3[T] \gg k_2$ and $d[T]/dt = -2k_1[T]$. At low diimide concentration, reaction 1 is always followed by reaction 2, $k_2 \gg k_3[T]$ and $d[T]/dt = -k_1[T]$. In each limiting case the decay of diimide is first order, with the rate constant decreasing from $2k_1$ to k_1 as the diimide concentration decreases from very high to very low values. This behavior is observed experimentally; Figure 2 shows the first-order rate constant decreasing from an initial value of 2×10^{-2} toward a final value of $\sim 1 \times 10^{-2}$ sec^{-1}.
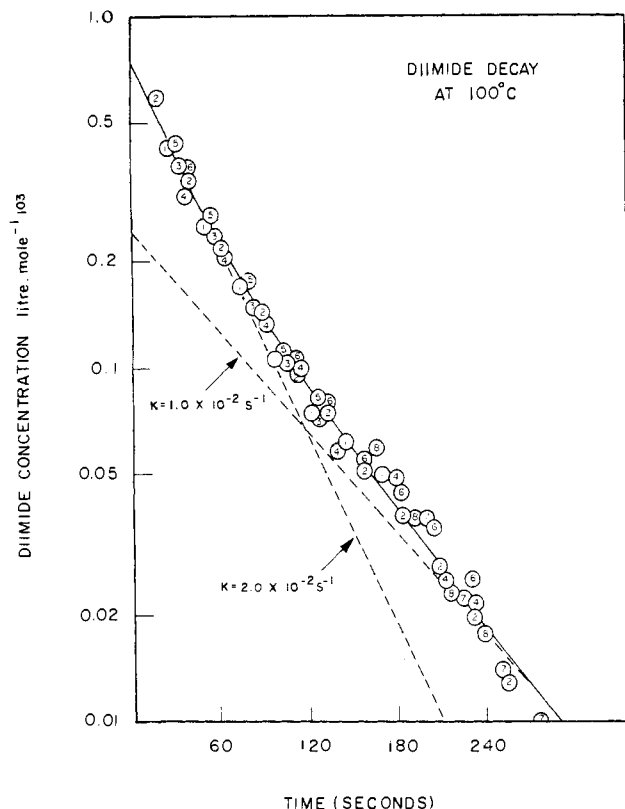
Figure 2. First-order plot of the decay of diimide in the gas phase at 100°. The results of eight separate experiments are combined, covering a 60-fold change in diimide concentration.
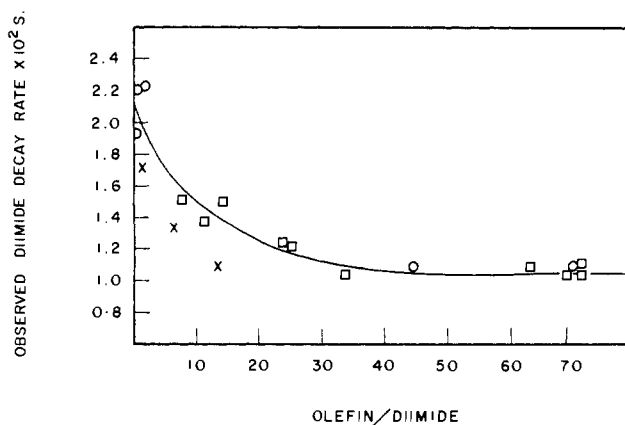

Figure 3. The effect of olefins on the initial rate of disappearance of diimide. The olefin:diimide ratio has been normalized as in Figure 5 to compensate for differences in reactivity: (O) ethylene; (□) *trans*-butene-2; (X) 1,3-butadiene.
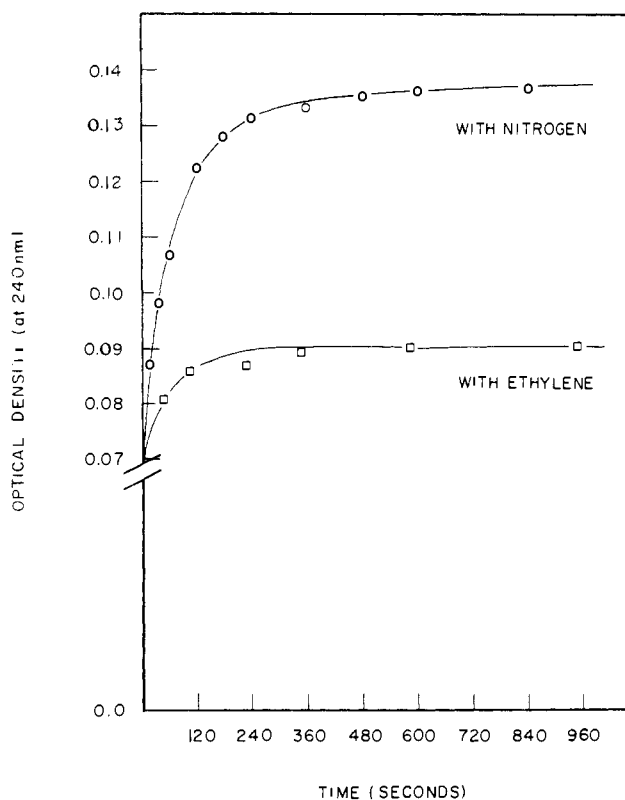

Figure 4. The effect of ethylene on the formation of hydrazine from the decomposition of diimide. The initial optical density of about 0.07 is due to absorption by hydrazine produced during the vaporization of diimide;[5] the increase in optical density above this value corresponds to hydrazine produced in the gas-phase reaction.

In the presence of a sufficiently high pressure of olefin, a third simple limiting condition is achieved in which reaction 1 is always followed by reaction 4; $k_4[\text{olefin}] \gg k_2 + k_3[\text{T}]$ and $d[\text{T}]/dt = -k_1[\text{T}]$. This accounts for the reduced initial rate of decay of diimide in the presence of olefin, shown in Figure 3; the rate constant is decreased from a value of about 2×10^{-2} sec^{-1} (corresponding to the "high diimide concentration" condition) to a value of about 1×10^{-2} at high pressure of olefin.

The competition between reactions 3 and 4 is also demonstrated by the effect of olefins on the yield of hydrazine (Figure 4), discussed previously. These data are in good accord with the proposed mechanism but do not yield accurate rate constants because of uncertainty in the diimide concentration, which was not measured in these experiments.

From the mechanism, an expression can be derived for the observed dependence of the yield of reduction product on the ratio of olefin to initial diimide concentration, shown in Figure 1. If reaction 2 is neglected and olefin concentration assumed constant in the reaction, by taking the ratio of $d[\text{reduction product}]/dt$ and $d[\text{T}]/dt$, integrating, and dividing by $[\text{T}]_0$ we obtain

$$\frac{[\text{reduction product}]}{[\text{T}]_0} = \frac{k_4}{2k_3}\left(\frac{[\text{olefin}]}{[\text{T}]_0}\right) \ln \left[1 + \frac{2k_3}{k_4}\left(\frac{[\text{T}]_0}{[\text{olefin}]}\right)\right] \quad (6)$$

where $[\text{T}]_0$ is the initial concentration of *trans*-diimide. It is clear from this expression that the fractional yield of reduction product should be a unique function of the [olefin]:[T]$_0$ ratio, independent of absolute value of $[\text{T}]_0$, as is observed (Figure 1). Reaction 2 can apparently be neglected even at low [olefin]:[T]$_0$ ratios largely because the rate constant for

reaction 2 appears only in the log term, and there in both numerator and denominator, tending to partially cancel.

It is also clear from eq 6 that the intrinsic shape of the curves in Figure 1 should be the same for all olefins and that by applying normalizing factors to the values of the olefin concentration to compensate for variation in k_4, the data for all the olefins should be brought to lie on a single curve. This is shown in Figure 5 where it is seen that within the experimental scatter the data for the four olefins are indistinguishable. From the normalization factors, relative values of k_4 can be obtained and are shown in Table I. Values for 2,3-dimethylbutene-2 and cyclohexadiene are also included; these are much less accurate because of their
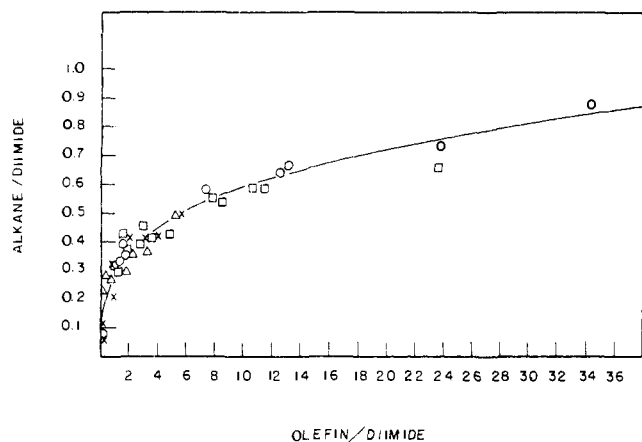
Figure 5. Normalized combined plot of the data from Figure 1. The olefin:diimide ratio for each olefin has been normalized to give the best fit to the curve for ethylene: (O) ethylene; (□) trans-butene-2; (△) cis-butene-2; (X) 1,3-butadiene.

low reactivity and because their low volatility did not permit high [olefin]:[T]$_0$ ratios to be used.

Also listed in Table I is an estimate of the relative rate of reaction of cis-diimide with trans-diimide, reaction 3. This

Table I. Reactions of cis-Diimide

Substrate	Relative rate ($C_2H_i = 1.00$)	Product
trans-Diimide	4–8	Hydrazine
Ethylene	1.00	Ethane
trans-Butene-2	0.33 ± 0.03	n-Butane
cis-Butene-2	0.11 ± 0.01	n-Butane
1,3-Butadiene	0.065 ± 0.007	Butene-1
1,3-Cyclohexadiene	$\sim 0.05 \pm 0.02$	Cyclohexene
2,3-Dimethylbutene-2	$\sim 0.02 \pm 0.01$	2,3-Dimethylbutane

was derived from a suitable plot of eq 6, using data from experiments with both ethylene and butadiene. The equation is inherently insensitive to the value of k_3/k_4, but it can be concluded that at 100°, reaction with trans-diimide is between 4 and 8 times faster than reaction with ethylene. At room temperature, it is clear that the reaction with olefins competed much less effectively with reaction 3, indicating a lower activation energy for the latter.

The trend observed in the relative reactivities is the reverse of that expected for free-radical reactions (e.g., H atoms) with olefins, which should be most rapid with the dienes.[11] Neither does it resemble reaction of electrophillic species such as ozone or $O_2(^1\Delta)$, which would be most reactive toward 2,3-dimethylbutene-2.[12] The trend of reactivities suggests instead that cis-diimide is behaving like a diene in a Diels–Alder reaction, with the olefins showing typical dienophile behavior.[13] This in turn suggests a reaction proceeding through a six-membered transition state

$$\begin{array}{c} /\ \backslash \\ -C==C \\ H \quad\ \ H \\ N==N \end{array}$$
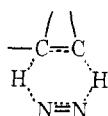
with synchronous transfer of both hydrogens from the reactive cis isomer of diimide to the olefin. Similar suggestions have been made to explain relative reactivities and the stereospecificity of hydrogenation by diimide in solution.[4,6,14]

We have no evidence for participation of diimide in cy-

cloaddition reactions with the olefins, either a Diels–Alder reaction with the dienes (in which N_2H_2 would react as the mono-ene) or addition to the simple olefins comparable to the very efficient dioxetane formation[12,15] in the reaction of $O_2(^1\Delta)$ with 2,3-dimethylbutene-2. Mass spectrometric analysis of reaction mixtures showed no products of such reactions; detection of the expected unknown cyclic hydrazines or their decomposition products could, however, be difficult. The alkane yields (Figures 1 and 4) and the kinetic data (Figure 3) are incompatible with the occurrence of a major side reaction other than simple hydrogenation, but again, uncertainty in the absolute extinction coefficient for diimide, and an insensitivity of the data to minor side reactions, make it impossible to rule out such reactions completely. The only known cycloaddition product of diimide is the anthracene adduct, prepared at reduced temperature by Mock;[6] it was observed to decompose to diimide and anthracene at about 80°, so it is perhaps not surprising that no evidence is found at 100° for cycloaddition to olefins known to be much less reactive than anthracene in such reactions.

Finally, it might be noted that a free-radical chain mechanism, propagated by H atoms and alkyl radicals, could be postulated for the reaction of diimide with the olefins, or indeed for the decomposition of diimide itself. The kinetics of the reaction and the relative reactivities of the olefins make such a mechanism untenable.

Conclusion

Diimide reacts fairly efficiently with olefins in the gas phase at 100° to yield simple hydrogenation products, approaching complete reaction at high pressures of olefin. The kinetics and stoichiometry of the reaction indicate that olefins do not react with trans-diimide, the "stable" isomer in the gas phase. It is suggested instead that the reacting species is cis-diimide and that the rate of reaction is controlled by the rate of isomerization, estimated to have a first-order rate constant of 1×10^{-2} sec^{-1} at 100°. The efficiency of the reaction with an olefin is determined by its rate relative to the competing decomposition of cis-diimide to $N_2 + H_2$ and its reaction with trans-diimide to yield $N_2 + N_2H_4$. The relative rates of reaction of the olefins suggest a concerted hydrogenation proceeding through a six-membered transition state. No evidence was found for any stable cycloaddition products of diimide with olefins.

References and Notes

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(2) NRCC Postdoctoral Fellow.
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(15) It is noteworthy that N_2H_2 in its singlet ground state is isoelectronic with $O_2(^1\Delta)$; its chemistry seems to be very different.