

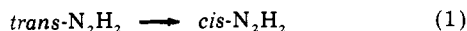
The Mechanism and Kinetics of the Reactions of Diimide with Unsaturated Compounds in the Gas Phase[†]

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Abstract: A detailed examination has been made of the gas phase reactions of diimide with a series of unsaturated compounds at 100 °C. Previous work had suggested a simple bimolecular hydrogenation by *cis*-N₂H₂ but competition experiments involving pairs of unsaturates demonstrate that a much more complex mechanism is operative. It is speculated that a transient adduct is formed, probably a π* complex between *cis*-N₂H₂ and the unsaturate, which can either undergo a rearrangement to yield the hydrogenation products or can hydrogenate a second species, *trans*-N₂H₂ or another unsaturate. A notable observation is that oxygen shows no reactivity toward *cis*-N₂H₂.

In an earlier paper¹ we proposed the following mechanism for the gas phase reaction of diimide, N₂H₂, with unsaturated hydrocarbons.



Yields of hydrogenated product from a series of olefins were measured as a function of olefin/diimide ratio. Normalization factors were applied to fit the data for all the olefins to a single curve, from which relative rate constants for reaction with diimide were obtained. Although the results could be fitted to this simple mechanism, there were some inconsistencies with earlier work. In particular, 1,3-butadiene had been shown² to be *very efficient* in suppressing hydrogen formation in the room temperature decomposition of diimide, whereas at 100 °C it was found¹ to be *very inefficient* in reacting to form hydrogenated products. The present paper reports a much more detailed examination of the stoichiometry, reaction rate, and mechanism of the reaction of diimide with unsaturated additives. As will be seen, a more complex mechanism is required to explain all the features of the reaction and this may have significant implications on the use of diimide, generated in situ, for stereospecific hydrogenation.³

Experimental Section

Preparation of Diimide. N₂H₂ was prepared by microwave decomposition of hydrazine vapor as described earlier.^{1,2} Samples were rapidly vaporized into the reaction vessel by warming with hot water. In most experiments diimide was introduced first, followed by the reactant; in a few experiments the reverse sequence was used. No differences were observed which could be attributed to the order of introduction.

Reaction Cells. Kinetic experiments and those involving measurement of N₂, H₂, and N₂H₄ were carried out in a large, spherical quartz cell the contents of which could be simultaneously monitored by light absorption at two wavelengths.⁴ Experiments in which hydrocarbon products were analyzed were done in a small spectrophotometer cell (10 cm long, 2 cm i.d., Hellma Co. Ltd.); diimide was monitored by a single spectrophotometer beam and the cell volume was small enough to allow the entire contents to be transferred to the inlet loop of a gas chromatograph.

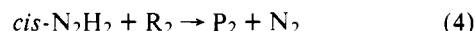
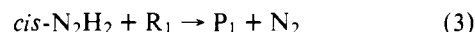
Analyses. Diimide was monitored by its absorption at 365 nm⁵ using a molar decadic extinction coefficient⁴ of $\epsilon \pm 3.9 \pm 0.2$. Hydrazine was measured by its absorption at 240 nm using an extinction coefficient⁴ at 100 °C of $\epsilon \pm 78$. Hydrocarbon products were identified and measured by gas chromatography with flame ionization detection. N₂ and H₂

were measured by gas buret and the proportion of H₂ was determined by diffusion through a hot palladium thimble.

Results

All experiments were carried out at 100 °C unless otherwise noted, and at pressures greater than 200 Torr. Earlier work⁴ had shown rates to be pressure dependent at lower pressures. Olefins were almost always present in sufficient excess that their consumption during the course of the reaction was negligible.

Yields of Hydrogenated Products. If the simple mechanism, reactions 1–3, were operative, the reaction of *cis*-N₂H₂ with two reagents, R₁ and R₂, would involve competition between the two reactions



where P₁ and P₂ are reaction products. Relative rate constants for reactions 3 and 4 could then be obtained from the reduction in the yield of P₁ by the addition of the second reagent, R₂:

$$\frac{P_1^0 - P_1}{P_1} \frac{R_1}{R_2} = \frac{k_4}{k_3} \quad (5)$$

P₁⁰ is the yield of P₁ when only R₁ is present. Relative rate constants could also be obtained if the yields of both products were determined:

$$\frac{P_2}{P_1} \frac{R_1}{R_2} = \frac{k_4}{k_3} \quad (6)$$

Determination of k_4/k_3 by both these methods⁶ should give values essentially identical with those determined by the method described earlier¹ and briefly recalled in the introduction, based on competition of single reagents with reaction 2.

Table I gives the results obtained using all three methods: relative rate constants obtained previously from normalization factors are reported as "relative efficiencies for producing hydrogenated product"; relative rate constants determined from eq 5 are reported as "relative efficiencies for suppressing ethane formation" from N₂H₂-C₂H₄ mixtures; and relative rate constants obtained from eq 6 are reported as "ratios of yields of hydrogenated products". Each value given is the mean of at least six different experiments.

If the simple mechanism previously proposed were correct, then all three "relative rate constants" should be equal; this is not so. Although the agreement is fair for certain reagents, for example, for *cis*- and *trans*-2-butene, for others there is a wide variation; for 1,3-butadiene the values vary by more than a factor of 1000.

[†] Issued as NRCC 16039.

Table I. Relative Efficiencies^a for Reaction of Diimide with Unsaturated Compounds

Reagent	Product(s)	Relative efficiency for producing hydrogenated product ¹	Relative efficiency for suppressing ethane formation ((E ₀ - E)/E), ([C ₂ H ₄]/[additive])	Products (P ₂ /P ₁)(R ₁ /R ₂)
Ethylene	C ₂ H ₆	1.00	1.00	1.00
Propene	C ₃ H ₈			1.01 ± 0.03
<i>trans</i> -2-Butene	<i>n</i> -C ₄ H ₁₀	0.33 ± 0.03	0.4 ± 0.1	0.61 ± 0.02
<i>cis</i> -2-Butene	<i>n</i> -C ₄ H ₁₀	0.11 ± 0.01		0.49 ± 0.03
Allene	C ₃ H ₆		1.0 ± 0.4	0.64 ± 0.02
Propyne	C ₃ H ₆		1.0 ± 0.4	0.62 ± 0.02
1,3-Cyclohexadiene	c-C ₆ H ₁₀	0.05 ± 0.02		
Benzene	c-C ₆ H ₈		>4	0.002
1,3-Butadiene	1-C ₄ H ₈	0.065 ± 0.007	>100	0.02 - 1.0
2,3-Dimethyl-2-butene	2,3-C ₆ H ₁₄	0.02 ± 0.01		0.44 ± 0.03
<i>trans</i> -N ₂ H ₂	N ₂ H ₄ , N ₂ , H ₂	4-8		
Azomethane	(CH ₃) ₂ N ₂ H ₂		3.0 ± 0.6	
Acetylene	C ₂ H ₄			0.36 ± 0.015
Cyclopropane	C ₃ H ₆		0.2 ± 0.2	0.0079 ± 0.004
Oxygen			0.0 ± 0.2	
Vinyl chloride ^b	C ₂ H ₅ Cl			
	C ₂ H ₄ + HCl			0.37 ± 0.03
Vinyl fluoride ^b	C ₂ H ₅ F			
	C ₂ H ₄ + HF			0.22 ± 0.01

^a All compounds are compared to ethylene. In some experiments where both hydrogenated products were determined, propene was used because it facilitated the gas chromatographic analysis. ^b Two product channels were observed for these additives. The ratio of channels was C₂H₅Cl/(C₂H₄ + HCl) = 11 ± 1, C₂H₅F/(C₂H₄ + HF) = 60 ± 10.

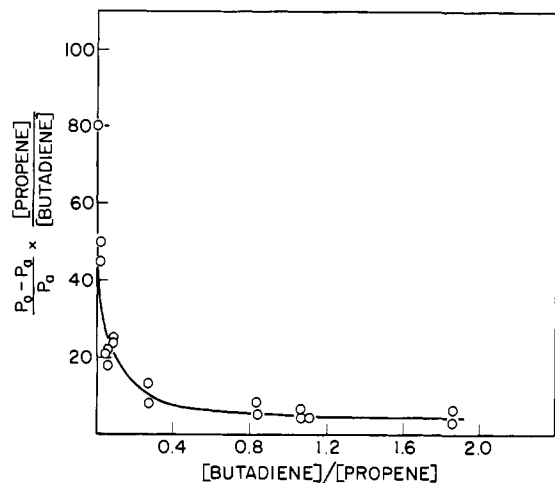


Figure 1. Efficiency of 1,3-butadiene for suppressing propane formation from propene-diimide mixture.

Butadiene-Propene-Diimide System. Because of the extreme behavior of 1,3-butadiene a detailed comparison of the results obtained from mixtures of propene and 1,3-butadiene is given in Table II.⁷ It is evident from the last two columns of this table that the relative yields of 1-butene and propane are a more complex function of propene and 1,3-butadiene concentration than is suggested by expressions 5 and 6. This is shown explicitly in Figures 1 and 2. In both these figures the function plotted should be independent of the [butadiene]/[propene] ratio if expressions 5 and 6 were applicable.

The complex behavior implied by these data indicates that propene and butadiene are not competing in a simple way for a single reactive species. This is demonstrated in Figure 3, which shows the variation of *total* yield of hydrogenated product, the propane yield plus the 1-butene yield, relative to that found from propene alone. The total yield of hydrogenated products clearly decreases as 1,3-butadiene is added.

Stoichiometry of Other Products. The fraction of N₂H₂ reacting to give (N₂ + H₂), (N₂ + N₂H₄), and (N₂ + alkane)

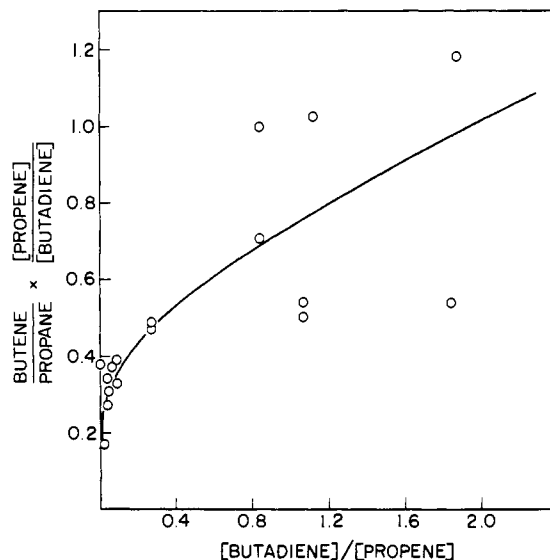


Figure 2. Ratio of yields of 1-butene and propane from propene-1,3-butadiene-diimide mixtures. The line drawn indicates no more than a possible trend.

as a function of olefin concentration is given in Figures 4 and 5 for propene and *trans*-2-butene. Qualitatively the results are similar. Addition of olefin reduces the H₂ yield toward a low value, perhaps zero, reduces the N₂H₄ yield to an apparent plateau value which is greater than zero, and increases the yield of alkane to a plateau value which is less than that expected if all the diimide reacted to form alkane. Previous experiments with ethylene¹ suggested that the reaction of ethylene with N₂H₂ to form ethane is completely efficient; the reactions of propene and *trans*-2-butene clearly are not.

With 1,3-butadiene present, N₂H₄ cannot be measured with reasonable precision because of spectral interference;⁸ its yield, however, can be inferred by mass balance from the initial amount of N₂H₂ and the yield of N₂. Although the yields given in Table III show considerable scatter, it is apparent that ad-

Table II. Yields from 1,3 Butadiene-Propene Mixtures^f

Initial propene, Torr	Initial butadiene, Torr	Initial diimide, Torr	Propane yield, Torr	Butene yield, Torr	[Butadiene]/[propene]	Rel propane yield	Rel butene yield	Rel total prod yield	((P ₀ - P)/[propene])/([butadiene]) ^e	(Butene/propane)/([propene]/[butadiene])
40.0	0.0	17.3	6.27		0.0	1.00 ^a	0.00 ^a	1.00 ^a		
80.0	0.0	16.3	7.94		0.0	1.00 ^b	0.00 ^b	1.00 ^b		
120.0	0.0	10.6	6.47		0.0	1.00 ^d	0.00 ^d	1.00 ^d		
119.7	0.76	10.8	4.35	0.01	0.0063	0.66 ^d	0.0016 ^d	0.66 ^d	80	0.38
40.5	0.26	14.7	2.77	0.01	0.0182	0.52 ^a	0.0016 ^a	0.52 ^a	50	0.17
119.1	2.3	14.3	4.62	0.03	0.0196	0.53 ^d	0.0035 ^d	0.53 ^d	45	0.34
40.0	0.78	26.2	5.03	0.03	0.0196	0.53 ^a	0.0028 ^a	0.53 ^a	45	0.27
39.5	1.6	18.2	3.56	0.04	0.0406	0.54 ^a	0.0067 ^a	0.55 ^a	21	0.31
120.3	7.0	10.7	3.20	0.07	0.0582	0.49 ^d	0.0106 ^d	0.50 ^d	17.6	0.37
39.5	2.3	17.2	2.74	0.04	0.0582	0.44 ^a	0.0068 ^a	0.45 ^a	22	0.27
119.4	10.4	10.1	1.97	0.07	0.0866	0.32 ^d	0.0109 ^d	0.33 ^d	24	0.39
80.8	7.0	12.9	1.95	0.06	0.0866	0.31 ^b	0.0090 ^b	0.32 ^b	25	0.33
120.7	32.5	14.6	2.76	0.44	0.269	0.31 ^d	0.0492 ^d	0.36 ^d	8.2	0.59
40.0	10.8	16.3	1.30	0.20	0.269	0.22 ^a	0.0336 ^a	0.25 ^a	13.2	0.57
119.9	100.9	15.2	1.67	1.02	0.841	0.18 ^d	0.1095 ^d	0.29 ^d	5.2	0.72
40.3	33.9	12.0	0.52	0.44	0.841	0.12 ^a	0.101 ^a	0.22 ^a	8.9	1.00
120.1	128.6	8.7	0.90	0.53	1.070	0.17 ^d	0.099 ^d	0.27 ^d	4.6	0.54
80.1	85.8	13.0	0.82	0.44	1.070	0.13 ^b	0.069 ^b	0.20 ^b	6.4	0.50
100.9	111.9	11.7	1.03	1.17	1.110	0.16 ^c	0.183 ^c	0.34 ^c	4.6	1.03
119.8	222.7	6.0	0.55	0.55	1.86	0.15 ^d	0.150 ^d	0.30 ^d	3.1	0.54
39.9	74.1	13.3	0.34	0.74	1.86	0.07 ^a	0.154 ^a	0.23 ^a	6.7	1.19

^a(Propane yield/initial N₂H₂)/(propane yield 40 Torr propene without 1,3-butadiene/initial N₂H₂). ^b(Propane yield/initial N₂H₂)/(propane yield 80 Torr propene without 1,3-butadiene/initial N₂H₂). ^c(Propane yield/initial N₂H₂)/(propane yield 100 Torr propene without 1,3-butadiene/initial N₂H₂). ^d(Propane yield/initial N₂H₂)/(propane yield 120 Torr propene without 1,3-butadiene/initial N₂H₂). ^eP₀ = propane, P = propane yield from mixture. ^fAll pressures in Torr at 100 °C.

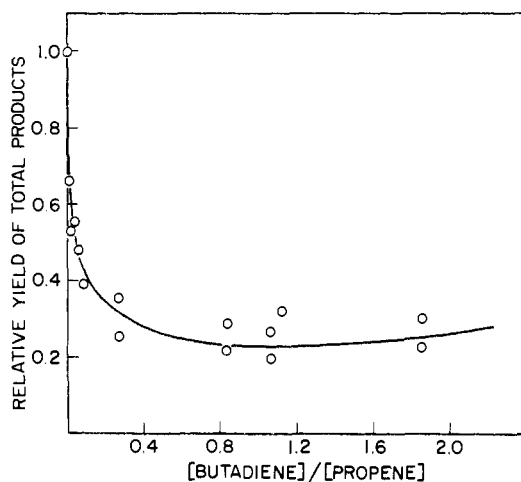


Figure 3. Total yield of propane and 1-butene, from propene-1,3-butadiene-diimide mixtures taken relative to propane yield from propene-diimide mixture.

dition of a small amount of 1,3-butadiene depresses the H₂ yield to zero and increases the N₂H₄ yield to close to that expected if all N₂H₂ decomposed to form N₂ + N₂H₄.

Kinetics of Disappearance of Diimide in the Presence of Added Reagents. The disappearance of diimide alone shows an initial faster than exponential decay which finally merges into simple linear first-order behavior. This initial curvature has been shown to be due to kinetic self-heating.⁴ As a consequence, meaningful kinetic results can only be obtained using the final linear portion of the decay. Since in each experiment the concentration of diimide decreases from some initial value to zero, this constrains kinetic observations to conditions where the added reagent is in considerable excess over diimide. Figure 6 shows the observed first-order decay rate constants of diimide in the presence of propene, *trans*-2-butene, and 1,3-butadiene. As might be expected with the reagents in large excess, there is no apparent dependence of decay rate on reagent concentration. The rates are very different, however, for the different

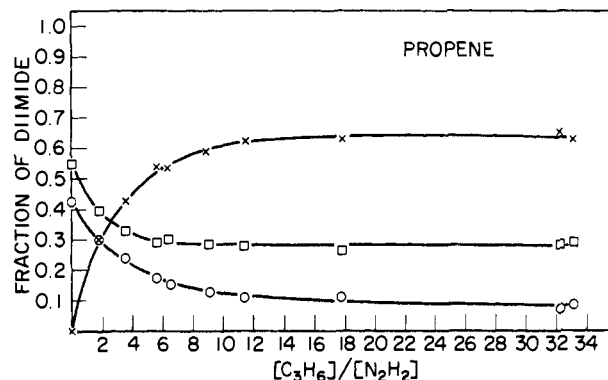


Figure 4. Stoichiometry of propene-diimide reaction: O, fraction of diimide reacting to give H₂ + N₂; □, fraction of diimide reacting to give N₂ + N₂H₄; X, fraction of diimide reacting to give N₂ + propane (inferred from mass balance knowing amount of diimide reacted).

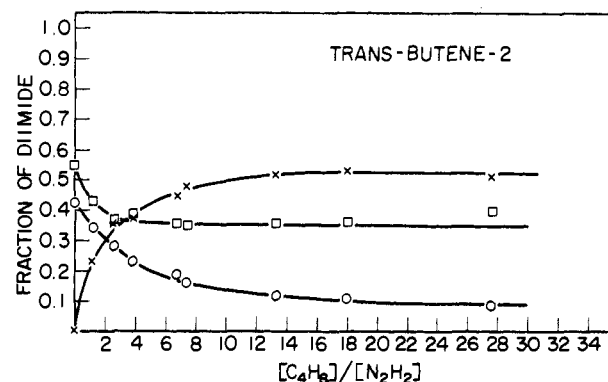


Figure 5. Stoichiometry of *trans*-2-butene-diimide reaction: O, fraction of diimide reacting to give H₂ + N₂; □, fraction of diimide reacting to give N₂ + N₂H₄; X, fraction of diimide reacting to give N₂ + butane (inferred from mass balance knowing amount of diimide reacted).

olefins. At 100 °C the first-order rate constant for decay of diimide alone⁴ is approximately 1 × 10⁻² s⁻¹; propene leaves

Table III. Stoichiometry of Reaction of 1,3-Butadiene and Diimide^e

Initial pressure butadiene, Torr	Initial pressure diimide, Torr	Yield N ₂ , Torr	Yield H ₂ , Torr	Yield N ₂ H ₄ , Torr ^a	[Butadiene]/[diimide]	Fraction of N ₂ H ₂ reacting to N ₂ + N ₂ H ₄ ^b	Fraction of N ₂ H ₂ reacting to N ₂ + H ₂ ^c	Fraction of N ₂ H ₂ reacting to N ₂ + butene ^d
0.0						0.65	0.35	
19.33	8.12	3.91	0.30	3.91	1.7	0.96	0.04	-0.04
51.85	9.38	4.65	0.33	4.53	3.9	0.97	0.03	-0.02
19.82	3.14	1.42	0.06	1.54	4.4	0.98	0.02	-0.06
104.46	8.56	4.81	0.18	4.19	8.6	0.98	0.02	+0.05
134.30	9.28	4.95	0.04	4.62	10.2	0.99	0.01	+0.03
115.95	5.58	2.79	0.13	2.73	14.6	0.98	0.02	-0.01
120.46	3.73	1.88	0.08	1.83	22.8	0.98	0.02	-0.01
219.15	5.48	2.70	0.06	2.71	28.1	0.99	0.01	-0.01
226.97	5.58	2.91	0.11	2.74	28.6	0.98	0.02	+0.01

^a Calculated from mass balance $N_2H_4 = (N_2H_2 - H_2)/2$. ^b Calculated from N₂H₄ yield, fraction = $(2 \times N_2H_4)/N_2H_2$. ^c Calculated from H₂ yield, fraction = H_2/N_2H_2 . ^d Calculated from mass balance, fraction = $(N_2 - N_2H_4 - H_2)/N_2H_2$. ^e All pressures in Torr at 100 °C.

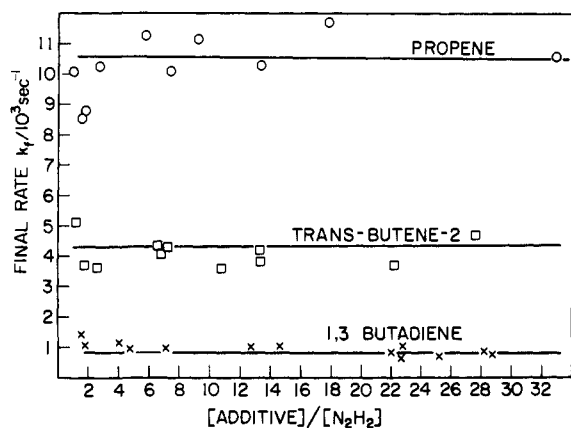


Figure 6. Rate of disappearance of diimide derived from final first-order portion of decay: O, added propene; □, added *trans*-2-butene; X, added 1,3-butadiene.

this unchanged, *trans*-2-butene reduces it by a factor of approximately 3, and 1,3-butadiene reduces it by a factor of 12.

Figure 7 shows the decay rate constant of diimide in the presence of 1,3-butadiene as a function of temperature, plotted in Arrhenius form. The line drawn gives the rate expression

$$\log k \text{ (s}^{-1}\text{)} = 0.255 - (5700/4.575T)$$

which should be compared to the rate expression observed for diimide decay in the absence of additives:⁴

$$\log k \text{ (s}^{-1}\text{)} = 0.477 - (4300/4.575T)$$

Discussion

The reaction of diimide with unsaturated hydrocarbons is clearly much more complex than previously suggested.¹ Before relative rate constants can be assessed, it is necessary to consider possible reaction mechanisms which are consistent with the present results.

Mechanism of Reaction. Diimide is formed predominantly as the *trans* isomer.^{1,2,5} In a recent paper⁴ we concluded that the thermal decomposition was initiated by a gas phase isomerization yielding *cis*-N₂H₂ which then reacted rapidly with *trans*-N₂H₂ to form the products observed, N₂ + N₂H₄ and N₂ + H₂. There was no evidence for the participation of free radicals, a conclusion strongly supported by photochemical studies⁹ in which a radical chain does occur giving very different decomposition products. Further supporting evidence comes from the effect of added oxygen. Small amounts of

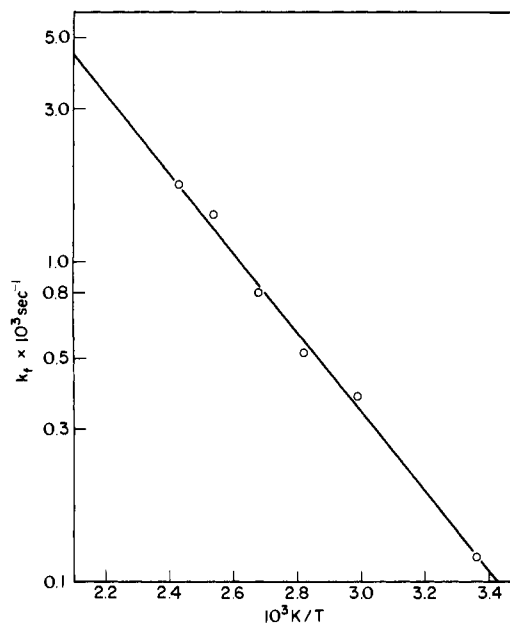
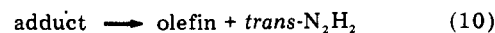
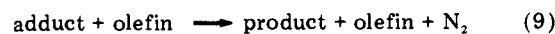
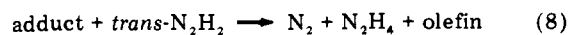
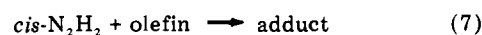
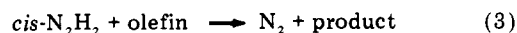
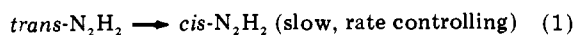


Figure 7. Arrhenius plot of rate of disappearance of diimide in 1,3-butadiene-diimide mixtures.

oxygen suppress the photochemical formation of C₂H₆ from N₂H₂-C₂H₄ mixtures, while addition of oxygen does not affect C₂H₆ formation from the thermal reaction (see Table I).

The following mechanism is qualitatively consistent with the experimental observations:



The dependence on olefin concentration of H₂ formation, N₂H₄ formation, and product formation can now be different. Suppression of H₂ will depend on the rate of reaction 2 relative to 3 and 7; product formation will depend on the rates of reactions 3 and 9 relative to reactions 7, 8, and 10. Hydrazine will show a different concentration dependence as it can be formed either by reaction of *cis*-N₂H₂, reaction 2, or by reaction of adduct, reaction 8. Thus propene can be relatively inefficient

Table IV. Rate Constants Derived from Numerical Simulation of Reaction of Diimide with Olefins

No.	Reaction	Reaction rate constant (2nd order units $M^{-1} s^{-1}$)			Footnote
		Propene	Butene	Butadiene	
1	$trans\text{-}N_2H_2 \rightarrow cis\text{-}N_2H_2$	1×10^{-2}	1×10^{-2}	1×10^{-2}	<i>a</i>
2a	$cis\text{-}N_2H_2 + trans\text{-}N_2H_2 \rightarrow N_2H_4 + N_2$	5.1×10^5	5.1×10^5	5.1×10^5	} <i>b</i>
2b	$cis\text{-}N_2H_2 + trans\text{-}N_2H_2 \rightarrow N_2 + H_2 + trans\text{-}N_2H_2$	8.4×10^5	8.4×10^5	8.4×10^5	
3	$cis\text{-}N_2H_2 + olefin \rightarrow N_2 + product$	9.9×10^4	5.8×10^4	Slow	} <i>c</i>
7	$cis\text{-}N_2H_2 + olefin \rightarrow adduct$	1.5×10^4	1.8×10^5	Very fast	
8	$adduct + trans\text{-}N_2H_2 \rightarrow N_2 + N_2H_4 + olefin$	9.0×10^5	9.0×10^5	9.0×10^5	} <i>d</i>
9	$adduct + olefin \rightarrow product + olefin + N_2$	Slow	Slow	?	
10	$adduct \rightarrow olefin + trans\text{-}N_2H_2$	0.0	4.5×10^3	$\geq 3 \times 10^4$	

a Reference 4. *b* The value of $k_{2a} + k_{2b}$ is derived relative to k_3 and k_7 . The ratio of k_{2a}/k_{2b} is based on relative yields of products. *c* The values of k_3 and k_7 are derived from the relative plateau values. *d* Including this reaction does not improve the fit for the propene and butene results but it is probably required for the butadiene system; see text.

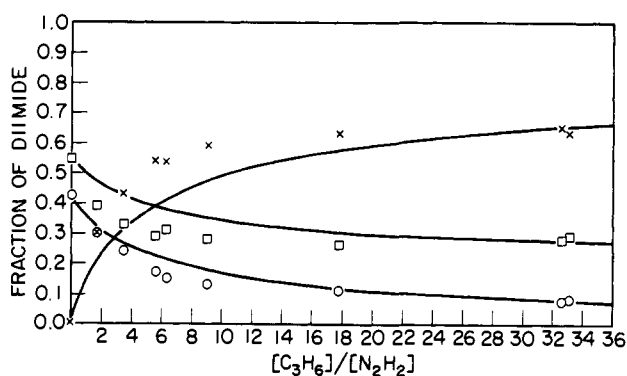


Figure 8. Calculated fit of mechanism to observed stoichiometry for propene-diimide mixtures: —, calculated values; O, fraction of diimide reacting to give $H_2 + N_2$; □, fraction of diimide reacting to give $N_2 + N_2H_4$; X, fraction of diimide reacting to give $N_2 + propane$.

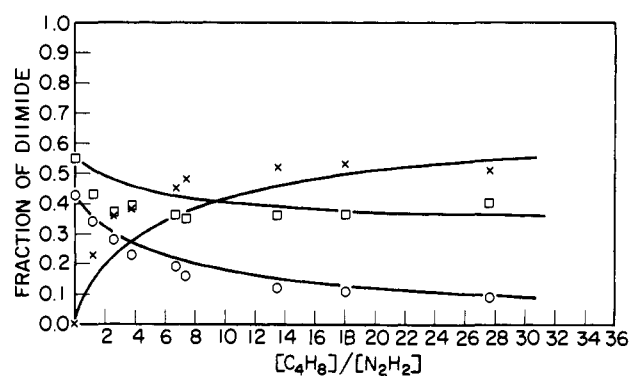


Figure 9. Calculated fit of mechanism to observed stoichiometry for *trans*-2-butene-diimide mixtures: —, calculated values; O, fraction of diimide reacting to give $H_2 + N_2$; □, fraction of diimide reacting to give $N_2 + N_2H_4$; X, fraction of diimide reacting to give $N_2 + butane$.

in suppressing H_2 but efficient in producing propane while 1,3-butadiene can be very efficient in suppressing H_2 yet very inefficient at forming 1-butene, leading preferentially to formation of N_2H_4 by reaction 8 instead. In this way the addition of butadiene to propene-diimide mixtures can reduce the total yield of hydrogenated olefin (Figure 3).

Reaction 9 is included in the mechanism because the shapes of the curves in Figure 1 and Figure 3 suggest that the butadiene-diimide adduct is capable of hydrogenating a second olefin molecule presumably by a reaction similar to that of reaction 8. However, inclusion of reaction 9 does not significantly improve the calculated fit of the mechanism to the experimental data for propene and 2-butene.

Both butene and butadiene lead to a significant reduction in the rate of disappearance of diimide (see Figure 6). If the isomerization step, reaction 1, is indeed rate controlling, then a reaction is needed in the mechanism to re-form *trans*- N_2H_2 . Reaction 10 will have the effect of apparently reducing the rate of reaction 1, thereby leading to a reduction in the rate of disappearance of diimide.

An explicit kinetic analysis of the proposed mechanism is complex. Since the concentration of diimide changes from an initial value to zero in each experiment, solution by inspection is impossible. The experimental results have been simulated by numerical analysis which integrates numerically each of the elementary reactions over the entire course of the experiment. We used a shortened version of a program by DeTar¹⁰ which allows for steady state concentrations of designated intermediates. The fit to the propene and butene data is shown in Figures 8 and 9 using the rate data given in Table IV. The precision of the fit is fair at higher concentrations of olefin but poor at low concentrations. We have been unable to signifi-

cantly improve the fit with the proposed mechanism. This discrepancy may be due to the kinetic self-heating effect⁴ previously mentioned. As more and more olefin is added, the temperature rise due to self-heating is reduced, so that at low concentrations the effective temperature of reaction is higher than at high concentrations. If, as suggested by preliminary work,^{1,3} there is a significant activation energy for reaction of *cis*- N_2H_2 with olefins, low concentrations of olefin will be anomalously effective.

We have not exhaustively searched for a closest fit: this would have been tedious and of dubious value given the number of unknowns and the possible effects of self-heating. The fit obtained, however, indicates that the proposed mechanism does have the necessary properties to explain most of the experimental observations.

Relative Reactivities in the Reactions of *cis*- N_2H_2 with Unsaturates. In a recent study of the decomposition of diimide itself,⁴ we suggested that the two reaction paths of *cis*- N_2H_2 with *trans*- N_2H_2 , reactions 2a and 2b, proceeded by interaction of the hydrogen atoms and the n orbital, respectively, of *cis*- N_2H_2 with the π - π^* system of *trans*- N_2H_2 ; i.e., the two paths corresponded to interaction in the same plane but on opposite sides of the *cis*- N_2H_2 molecule. Reaction 2a was envisaged as a simple direct concerted hydrogenation (such as Woodward and Hoffmann¹¹ use as a classic example of an allowed group transfer), while it was suggested that reaction 2b occurred through a transient n - π^* complex. It can be seen that the mechanism we are suggesting for the olefin reactions is closely similar, with reactions 3 and 7 corresponding to reactions 2a and 2b, the chief difference being that the adduct in some cases at least must be stable enough to undergo such

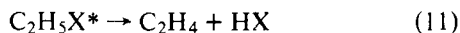
reactions as 8 and 9. Again, the structure of the adduct is most probably a $n^- - \pi^*$ complex, for the same reasons as discussed in the diimide system, as $\pi - \pi$ four-center interactions will tend to have high activation energies.

If this picture of the reaction of olefins with diimide is correct, the relative reactivities reported previously¹ and shown in column 3, Table I, will be largely a measure of reaction 3, the simple direct hydrogenation, with relatively small contributions from reaction 9, and our earlier discussion about these reactions and the dienophile behavior of the olefins remains for the most part valid.¹ The reactivities shown in column 4 will correspond approximately to a sum of reactivities via reactions 3 and 7, while those in column 5 will represent a more complex combination of the two. The order of reactivities for adduct formation (reaction 7) evident from columns 4 and 5 tends to be almost the reverse of those for simple hydrogenation. This is perhaps most notable for 1,3-butadiene and benzene, which are both very inefficient in undergoing hydrogenation, but highly reactive in adduct formation. The high reactivity of 1,3-butadiene suggests that 1,4-cycloaddition might be occurring, but a careful search for the product, 1,2,3,6-tetrahydropyridazine, which should be stable,¹² was unsuccessful, and the mass balance in the butadiene system rules out major formation of addition products.

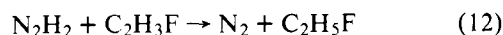
The low reactivity of oxygen has already been discussed briefly. It is in direct contrast to the observation of Wiberg and co-workers, who report¹³ that gaseous oxygen reacts with N_2H_2 in the solid state at temperatures as low as $-196^\circ C$ to form H_2O_2 and N_2 . This and other differences between our work and that of Wiberg and co-workers have been discussed elsewhere.⁴ Although no really satisfactory explanation is available at present, it is possible that different isomers of N_2H_2 are involved in the two sets of experiments. It is interesting to note that oxygen does not reduce product yields when diimide, generated in situ from azodicarboxylate, is used to hydrogenate unsaturated sites in solution.¹⁵

The very low relative rate for reaction of cyclopropane with diimide is in agreement with the solution behavior of diimide generated in situ which is used to reduce unsaturated centers without attack on neighboring cyclopropane rings.¹⁶ The small yield of propane which is observed from cyclopropane raises some interesting mechanistic questions but these are beyond the scope of the present paper.

The observation of two product channels in the reaction of diimide with vinyl chloride and vinyl fluoride is interesting. Elimination of HX from vibrationally excited haloethanes



is well known and offers the most probable mechanism for ethylene formation from the vinyl halides. The calculated activation energy for HF elimination from C_2H_5F is 57 kcal mol⁻¹.¹⁷ Hydrogenation of vinyl fluoride by diimide



is exothermic by 68 kcal mol⁻¹;¹⁸ there is thus sufficient energy for HF elimination provided that N_2 is formed with little vibrational excitation and provided that loss to translational energy of the products is small. The energetics of HCl elimination from the reaction of diimide with vinyl chloride are very similar to those for vinyl fluoride.

Conclusion

The mechanism of the reaction of diimide with unsaturated compounds has been shown to be rather more complex than had been suggested earlier. It is speculated that in addition to direct hydrogenation by *cis*- N_2H_2 , adducts can be formed which can lead to hydrogenation, to hydrazine formation, or to regeneration of trans diimide. Diimide has been used fairly extensively as a stereospecific hydrogenation reagent in organic synthesis³ and more recently the yields of this reaction have been used to derive information on ring strain phenomena.¹⁹ The complexity of the mechanism revealed in the present study should introduce a note of caution into some of these interpretations.

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