

THE PHOTOCHEMICAL DECOMPOSITION OF DIIMIDE IN THE GAS PHASE*

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Summary

The photodecomposition of *trans*-diimide, N_2H_2 , in its $\pi^* \leftarrow n_+$ absorption band has been studied in the gas phase at room temperature at wavelengths from 310 to 405 nm, both in the presence and absence of ethylene. Free-radical chain mechanisms are operative in both systems, yielding $N_2 + C_2H_6$ in the presence of ethylene and $N_2 + H_2$ in its absence. It is concluded that the primary photodissociation probably occurs from high vibrational levels of the ground state, reached by rapid intersystem crossing directly from the 1B_g state originally excited. There is no evidence for collisional de-excitation, and dissociation into $N_2H + H$ or $N_2 + 2H$ probably occurs with a quantum yield close to unity, although some molecular dissociation into $N_2 + H_2$ cannot be excluded. There is some evidence that N_2H radicals have appreciable stability in the chain reaction systems at room temperature.

Introduction

The photochemistry of the azoalkanes has been the subject of repeated study for a number of years [1], and the main steps in the photodecomposition have been shown to be:



followed largely by:



The details of the intermediate photophysical processes which may be involved in reaction (1), however, are not yet fully understood. There is no luminescence [1], but there is good evidence for the collisional deactivation of excited intermediates, and studies of the effect of pressure on quantum yields

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of dissociation and more recently of the concomitant *cis-trans* isomerization, have yielded considerable information [2 - 4]. Notably Fogel and Steel [4] have reported a comprehensive study of the photolysis and thermolysis of *trans*- and *cis*-azoisopropane from which they concluded that both isomers photodecompose through a common excited intermediate. From a comparison of the pressure dependences of the quantum yields in the direct photolysis, the photosensitized decomposition, and the thermolysis, with the prediction of unimolecular decomposition theory, they were able to show that this common intermediate was a vibrationally excited ground-state molecule, disproving earlier conclusions that vibrationally excited (π^* , n) states were involved [2, 3].

trans-Diimide, N_2H_2 , may be regarded as the prototype azoalkane. Contrary to earlier speculation, it has been shown to have appreciable stability in the gas phase at room temperature, decomposing with a half-life of a few minutes to N_2 , H_2 , and N_2H_4 by a non-radical mechanism [5]. Unlike the simple (non-cyclic) azoalkanes, its spectrum in the near ultra-violet shows considerable structure and a vibrational analysis is possible [6]. The spectrum is consistent with a symmetry-forbidden $\pi^* \leftarrow n_+$ transition made partially allowed by vibronic interaction. Excitation causes a large increase in the H-N-N angle and a small increase in the N-N bond length. These changes are consistent with the assignment and agree, at least qualitatively, with most theoretical predictions [7].

The photochemistry of diimide has not been studied before except for a few qualitative experiments at very low pressure by Wiberg [8] who reported that the photolysis produced N_2 and H_2 . The thermal instability of diimide makes a quantitative study somewhat difficult, but because of its importance to an understanding of the photochemistry of azo compounds in general, such a study was undertaken. The present paper reports our findings.

Experimental

Preparation of diimide

A sample of N_2H_2 together with a five to six fold excess of NH_3 was prepared for each experiment by passing hydrazine vapour through a weakly coupled microwave discharge [5]. The sample was collected in a U-tube at $-196^\circ C$ and rapidly vapourized into the photolysis cell by warming with hot water.

Photolysis apparatus

The cylindrical quartz photolysis cell was 20 cm long with a diameter of 3.5 cm and a volume of 180 ml. Two different light sources were used: (i) a 1000 W xenon arc interfaced with a Scoeffel 0.5 m monochromator, with a Pyrex filter to eliminate scattered light below 300 nm; (ii) a 500 W medium-pressure mercury arc with a Hanovia 3650 interference filter which selects the group of lines at 365 nm. These rather intense light sources were required

so that the photolysis of the diimide could compete effectively with its thermal decomposition; the latter goes to completion in a few minutes, and the absorption is weak.

The transmitted light intensity, and from this the concentration of diimide, was monitored by a photomultiplier, using several neutral-density filters to avoid saturation. Blank runs (to measure products of the thermal decomposition) were made with the neutral-density filters placed between the light source and the cell, while photolysis experiments were made with the filters between the cell and the photomultiplier. Incident intensities were varied by varying either the monochromator slit width or the position on the neutral-density filters.

The total light absorbed during the course of an experiment was determined by graphical integration of a plot of diimide disappearance. Actinometry was based on the yield of N_2 from the photolysis of azomethane (10 - 20 Torr) assuming a quantum yield of unity [1]. The integrated absorbed light was measured in each system, and was corrected for the wavelength dependence of the IP21 photomultiplier sensitivity, the incident light intensity, and the extinction coefficients of diimide and azomethane. Less than 10% of the incident intensity was absorbed at the start of any experiment, and the absorption decreased rapidly with time; diimide, of course, was completely consumed in each experiment.

Analysis

The amount of N_2H_2 in the cell was determined by its absorption of the incident light. At 365 nm a molar decadic extinction coefficient of 3.9 was used [5b]. The effective extinction coefficient at other wavelengths was estimated by comparison with the absorption at 365 nm in a crossed double beam apparatus described previously [5b].

The yields of N_2 and H_2 were determined by measurement in a gas burette and analysis for H_2 with a hot Pd thimble. Some diimide always decomposed in the transfer from the U-tube to the photolysis cell [5]. This was corrected for by analyzing the non-condensable products collected from a 50 ml bulb attached to the photolysis cell. The contents of this bulb were isolated and rapidly condensed at $-196^\circ C$ immediately after the diimide sample was introduced, before significant thermal reaction could occur. Knowing the ratio of the volumes of the photolysis cell and the bulb, proper correction for N_2 and H_2 formed during vaporization could be made [5a].

Yields of C_2H_6 and C_4H_{10} were determined by condensing the entire contents of the photolysis cell into the inlet system of a gas chromatograph equipped with a flame ionization detector. Peak heights were compared with those obtained with standard mixtures.

Results

Two main sets of experiments were performed. In the first, diimide was photolyzed in the presence of an excess of ethylene, and the yields of ethane

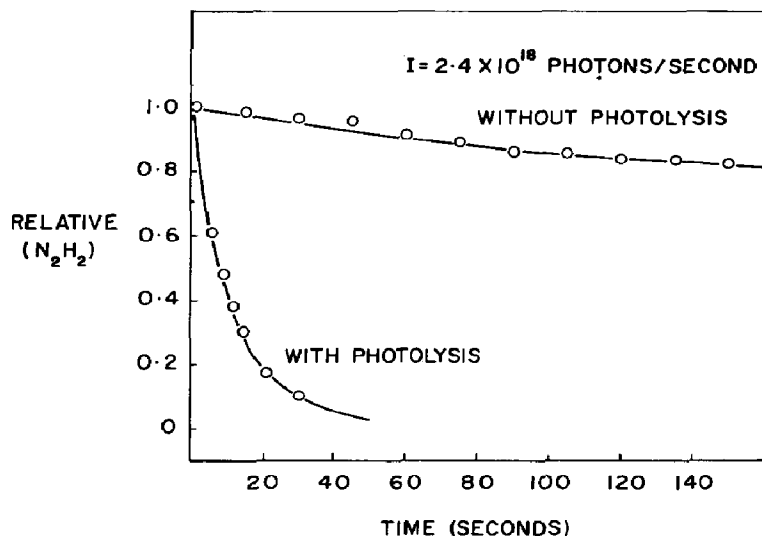


Fig. 1. Observed disappearance of diimide with and without photolysis.

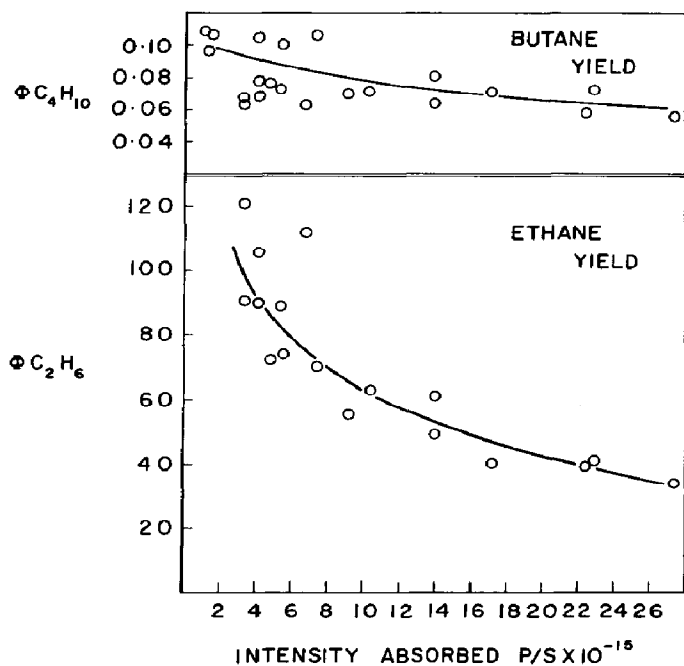


Fig. 2. Yields of ethane and butane from photolysis of $C_2H_4-N_2H_2$ mixtures as a function of absorbed intensity. The yields are corrected for contribution from thermal reactions.

and butane were determined. In the second, diimide samples were photolyzed without additive. Although the rate of production of diimide in the microwave discharge was somewhat erratic, approximately the same amount, about $100 \mu\text{mol}$, was used in each experiment.

TABLE 1

High intensity data for diimide photolysis*

Rate of absorption of light = $I_a = 1.3 \times 10^{-5}$ einstein $l^{-1} s^{-1}$ N_2H_2

$$[N_2H_2] = 2.5 \times 10^{-4} M$$

Quantum yield for diimide disappearance $\approx 18 \pm 8$ $N_2H_2-C_2H_4$

$$[N_2H_2] = 2.5 \times 10^{-4} M; [C_2H_4] = 1 \times 10^{-2} M$$

Quantum yield for diimide disappearance = 13 ± 6 Quantum yield of ethane = 7 ± 2 Quantum yield of butane = 0.05 ± 0.02 Rate of ethane formation = $R(C_2H_6) = I_a \cdot \Phi(C_2H_6) = 9 \times 10^{-5} M/s$ Rate of butane formation = $R(C_4H_{10}) = I_a \cdot \Phi(C_4H_{10}) = 6 \times 10^{-7} M/s$ * Values of I_a and N_2H_2 are approximate average values taken equal to 1/2 the initial values.

Photolysis in the presence of ethylene

As can be seen in Fig. 1, irradiation does markedly increase the rate of disappearance of diimide. In Fig. 2, quantum yields of ethane and butane are shown as a function of absorbed light intensity, using the xenon lamp with the monochromator. Ethane is also a product of the thermal reaction of diimide with ethylene [9], and the yields shown in Fig. 2 have been corrected for this, using the known stoichiometry and rate of the thermal reaction, and calculating iteratively the thermal contribution integrated over the course of the reaction. For the highest intensities this correction was small, less than 10%, but for lower intensities the correction becomes increasingly larger, leading to a much lower precision in the photochemical yields. No correction was required to the yields of butane as it is not a product of the thermal reaction [9].

Photolyses were carried out at wavelengths from 310 to 405 nm. No systematic variation of yields was observed other than that which could be attributed to variations in the absorbed light intensity. Results for all wavelengths are plotted together in Fig. 2.

The mercury arc with an interference filter gave a higher intensity than the xenon arc plus monochromator, and the mean values for the quantum yields at this intensity, at 365 nm, are given in Table 1 both for diimide-ethylene mixtures and for diimide alone. The quantum yield of ethane is smaller than that estimated for the disappearance of diimide, but the difference probably reflects only the experimental precision of the latter. The ratio of initial concentrations, C_2H_4/N_2H_2 was varied in the range 5 to 30 but had no effect.

The effect of small amounts of oxygen on the photolysis of $N_2H_2-C_2H_4$ mixtures is shown in Table 2. Addition of O_2 effectively eliminates the formation of butane and reduces the ethane yield. Because of the experimental

TABLE 2

Effect of adding O₂ on the yields of ethane and butane from the high intensity photolysis of C₂H₄-N₂H₂ mixtures

[C ₂ H ₄]/[O ₂]	Relative amounts detected	
	C ₂ H ₆	C ₄ H ₁₀
no O ₂	1.00	1.000
24/1	0.35	0.000
9/1	0.36	0.010
4/1	0.28	0.017

procedure necessary to prepare these 3-component reagent mixtures, accurate corrections for the thermal production of ethane were difficult to make, and the data shown are uncorrected. Oxygen has no effect on the thermal reaction of diimide with ethylene [9b], and if appropriate corrections are applied, the residual photochemical yields of ethane in the presence of oxygen appear to be very close to zero.

Photolysis of diimide in the absence of ethylene

The quantum yields for the disappearance of diimide cannot be determined with the same precision as those for ethane formation. It is seen in Table 1 that the quantum yield for the disappearance of diimide is approximately the same with and without ethylene present; certainly there is no dramatic change in behaviour. The products of the photolysis, of course, are very different. For the highest light intensities, when the thermal reaction was minimized, it was possible to demonstrate that the products of the photolysis were solely N₂ and H₂, with less than 3% of the original diimide decomposing to N₂H₄ + N₂. This is in direct contrast to the thermal decomposition, in which at room temperature 80% of the diimide decomposes to the latter products [5b]. The rate of disappearance of diimide in the photolysis was practically unaffected by the addition of oxygen.

Discussion

Mechanism of the photodecomposition

The main observations in the photolysis with and without ethylene may be summarized: (i) quantum yields of ethane are very much greater than unity and decrease with increasing absorbed light intensity; (ii) quantum yields of butane are much less than unity and independent of absorbed intensity; (iii) addition of O₂ suppresses the photochemical formation of ethane and butane; (iv) quantum yields of disappearance of N₂H₂ are about the same in the presence and absence of ethylene, and are approximately equal to that for the formation of ethane. These observations are consistent with a

radical chain mechanism in the photochemical decomposition of diimide both with and without ethylene present. From (i) and (ii) it follows that ethane must be produced in a chain propagation step, and if the primary quantum yield for radical production is close to unity, ethyl radical combination (which forms butane) cannot be the dominant termination reaction.

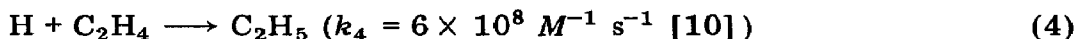
Because of the transient nature of diimide, the present study has some unusual experimental aspects which make a quantitative kinetic analysis of the results difficult. In each experiment the concentration of diimide and the percentage absorption of light decrease from their initial values to zero, so that the measured quantum yields are in fact averages over the time course of the experiment. Thermal reactions compete with the photolysis in a complex manner which depends on the light absorption and the diimide concentration, and the data are not sufficiently precise to accurately deconvolute the two systems. This allows only semi-quantitative conclusions to be drawn, but it will be seen that these are restrictive enough to determine the mechanism of the photolysis with some certainty, at least in the presence of ethylene. The corrections for thermal reactions are smallest for the results obtained at the highest intensity, which should thus be the most reliable, and only these data, shown in Table 1, have been used in calculations to test the proposed mechanism. The values shown are very approximate averages over the time course of the reaction, and the rate constants and radical concentrations obtained below are thus also very approximate.

Mechanism in the presence of ethylene

There can be little doubt that reaction (3) is the initiation step in the photolysis of diimide:



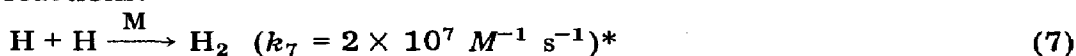
Whether one H atom or two are formed immediately is not important for the present discussion. When the pressure of ethylene is high enough, all H atoms will react to form ethyl radicals:



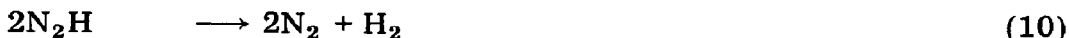
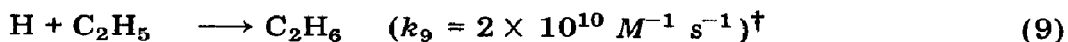
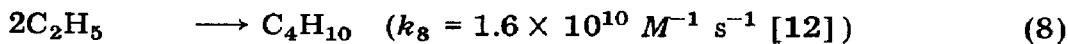
which will be followed by the reactions:



The reaction sequence, (4) (5) and (6), constitutes a chain reaction with the stoichiometry $\text{N}_2\text{H}_2 + \text{C}_2\text{H}_4 = \text{N}_2 + \text{C}_2\text{H}_6$. There are several possible termination reactions:



*This value of k_7 is the second-order rate constant at 200 Torr, the approximate pressure in these experiments, taking a third-body efficiency equal to that of H_2 [11].



Reaction (4) is to a good approximation always followed by reaction (5), since $\Phi(\text{C}_2\text{H}_6) \gg \Phi(\text{C}_4\text{H}_{10})$, and it will be seen that reaction (9) is negligible. The rate of formation of ethane will then be given by $R_{\text{C}_2\text{H}_6} = k_4 [\text{H}] [\text{C}_2\text{H}_4]$, and knowing k_4 , the steady state concentration of H atoms can be estimated as $[\text{H}] = 1.5 \times 10^{-11} \text{ M}$. It is easily shown then that reaction (7) is completely negligible as a termination step. The concentration of ethyl radicals can be estimated from the rate of formation of butane, since $R_{\text{C}_4\text{H}_{10}} = k_7 [\text{C}_2\text{H}_5]^2 \dagger\dagger$, from which $[\text{C}_2\text{H}_5] = 6 \times 10^{-9} \text{ M}$; combined with the value for [H] above, and a reasonable estimate of k_9 , it can also be shown that reaction (9) cannot be an important termination process.

A value of k_5 can also be estimated, since $R_{\text{C}_2\text{H}_6} = k_5 [\text{C}_2\text{H}_5] [\text{N}_2\text{H}_2]$, and for $[\text{C}_2\text{H}_5] = 6 \times 10^{-9} \text{ M}$ and $R_{\text{C}_2\text{H}_6} = 9 \times 10^{-5} \text{ M/s}$, $k_5 = 6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. This is of the same order of magnitude as the value of 1.3×10^7 recently estimated for the analogous reaction of methyl radicals with methyldiimide [13].

As noted earlier, the low quantum yield of butane implies that reaction (8) cannot be the main termination process if the quantum yield of reaction (3) is unity, and it has been seen that reactions (7) and (9) are not important. This points to N_2H as a terminating radical, either by reaction (10) or by combination with C_2H_5 radicals. Assuming reaction (10) to be the main termination step, a steady-state concentration of the N_2H radical can be estimated, and if reaction (10) has a normal fast rate typical of radical combination reactions of about $10^{10} \text{ M}^{-1} \text{ s}^{-1}$, then k_6 must have a value of about $3 \times 10^3 \text{ s}^{-1}$. This is very much smaller than an estimated rate constant for the analogous decomposition of the CH_3N_2 radical of about $3 \times 10^6 \text{ s}^{-1}$ at 22°C [13]. This implies a considerable stability for the N_2H radical, which at first sight is surprising since the NN-H bond dissociation energy is probably negative, estimated to be about -9 kcal/mol [14]. However, there could be a sizeable energy barrier for dissociation because the ground state of N_2H does not correlate with the ground states of N_2 and H, and Baird [14] has estimated an activation energy for decomposition of 22.6 kcal/mol . Assuming reaction (6) to have a pre-exponential term of 10^{13} s^{-1} , our estimated value of k_6 leads to an activation energy of 13 kcal/mol , which does not seem unreasonable.

[†]This is an estimated value.

^{††}This neglects formation of butane by other processes. It could be formed by the reaction sequence $\text{C}_2\text{H}_5 + \text{C}_2\text{H}_4 \rightarrow \text{C}_4\text{H}_9$, followed by $\text{C}_4\text{H}_9 + \text{N}_2\text{H}_2 \rightarrow \text{C}_4\text{H}_{10} + \text{N}_2\text{H}$, which from estimates of the rate constants might perhaps contribute to butane formation if the second reaction were very fast. Thus our estimate of $[\text{C}_2\text{H}_5]$ is an upper limit, which does not affect our conclusions about reaction (9).

The effect of oxygen on the diimide-ethylene photolysis system requires little comment. In direct contrast to the thermal reaction, the suppression of ethane and butane formation by oxygen strongly supports a radical chain mechanism for the photolysis and supports the earlier assumption that the thermal reaction does not involve radicals.

Mechanism in the absence of ethylene

The mechanism of the photolysis in the absence of ethylene is less clear. There are two possible reactions of H atoms with diimide:



If reaction (12) were occurring, one would expect the reaction:



to follow, and hydrazine would be a major product. Since this was not observed, it would appear that reaction (11) is the predominant reaction of H atoms with diimide, with the subsequent decomposition of N_2H by reaction (6) completing the chain sequence. It is possible, however, to propose an alternative chain reaction involving N_2H_4 . Hydrazine is initially present in the diimide samples, being formed by reaction during the transfer of the sample from the U-tube to the cell, with a concentration typically about 25 - 50% of the initial concentration of diimide. The reaction:



is relatively fast ($k_{14} = 1.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C [15]) and a chain giving N_2 and H_2 as products could proceed via reaction (14) followed by reactions (13) and (6). Without knowing the rate of reaction (12) it is not possible to decide between these two possible chain mechanisms. Accurate kinetic measurements of the rate of decomposition, which would be useful in determining the photolysis mechanism both with and without ethylene, were not possible because of the speed of the reaction and associated complications such as self-heating, finite mixing times, and others.

The approximate lack of effect of oxygen on the rate of disappearance of diimide in the photolysis in the absence of ethylene has some interesting implications. Either the reactions of oxygen with intermediates such as H, N_2H or N_2H_3 are too slow to compete with the normal reactions of these species, or the products formed, HO_2 for example, react with about the same efficiency to propagate the chain decomposition of diimide. Analysis for the effect of oxygen on production of N_2 and H_2 was not possible, and in its absence little more can be said.

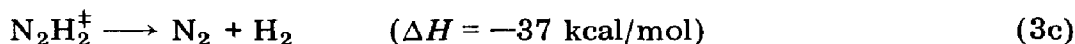
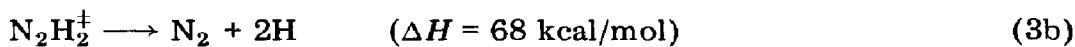
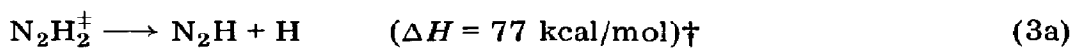
Photophysical processes in the photolysis, and the mechanism of the primary photodecomposition

The discussion to this point has dealt with the reactions following photodissociation, which was assumed to have a quantum yield of unity. It remains to consider the mechanism of the photodissociation itself.

Irradiation of *trans*-diimide in its first absorption region in the near u.v. excites a weak transition from the 1A_g ground state to the first excited singlet state, $^1B_g(\pi^* \leftarrow n_+)$ [6]. From the lack of rotational fine structure in the spectrum, it may be estimated that the lifetime of the excited state is less than 5×10^{-12} s. This lifetime is too short for fluorescence to have a significant yield in such a weak transition; diimide in this respect thus resembles the simple azoalkanes for which the quantum yield of fluorescence is less than 10^{-5} [1]. It also seems unlikely that intersystem crossing to the π^*-n_+ triplet state would be fast enough to be of any importance, and collisional quenching of the excited singlet state can also be ruled out.

In a recent paper on the photochemistry of azoisopropane, Fogel and Steel [4] suggested that in the azoalkanes, intersystem crossing occurs from the π^*-n_+ singlet state to highly excited vibrational levels of the ground state. For diimide it has been calculated that the potential surface of the 1B_g state comes very close to that of the ground state for 90° skew geometry, and that there is little or no barrier to rotation [7a]. Intersystem crossing thus could be very rapid, and appears to be the most probable fate of the 1B_g state in the photolysis. Decomposition of diimide would then occur from high vibrational levels of the ground state as suggested in the azoalkanes.

Three possible dissociation processes must be considered:



The formation of ethane and butane in the ethylene–diimide system is clear evidence for the occurrence of reaction (3a) or (3b) with a quantum yield of at least about 0.1. Of the two, reaction (3a) is much the more probable; while reaction (3b) is less endothermic, its activation energy is probably much higher because of a sizeable barrier to the reverse combination. Reaction (3c) is highly exothermic, but again a large barrier to the reverse combination can be expected. Direct formation of molecular products is not important in the other azoalkanes [17] but it could be more likely in diimide, the first member of the series (cf. formaldehyde [18]). Because H_2 is a product of the thermal decomposition, both during transfer from the U-tube and in the gas phase, it was not possible to determine whether photochemical formation of H_2 was totally suppressed by ethylene, or whether there was a residual yield which could be attributed to reaction (3c) (the fact that diimide disappears by a chain reaction minimizes primary products and makes their anal-

[†]The heats of reaction shown are for the dissociation of *trans*-diimide in its unexcited ground state, and are based on $\Delta H_f^\circ(N_2H_2) = 36 \text{ kcal/mol}$ [16] and $D(NN-H) = -9 \text{ kcal/mol}$ [14]. Note that the vibrationally excited ground-state diimide formed by intersystem crossing from the 1B_g state is probably a mixture of the *cis*- and *trans*-isomers [4]; this does not alter the overall energetics of the photodissociation, taking photoexcitation of *trans*- N_2H_2 in the ground state as the starting point.

TABLE 3

Mean quantum yields for butane formation as a function of photolyzing wavelength

Monochromator setting (nm)	Band pass (nm)	Butane yield $\Phi_{\text{C}_4\text{H}_{10}}$
325	15	0.061 \pm 0.003
345	8 - 20	0.075 \pm 0.017
365	8 - 20	0.070 \pm 0.08
	—	0.060 \pm 0.02*
380	10 - 20	0.069 \pm 0.09
400	15	0.089 \pm 0.10

*This was determined using Hg arc-filter combination: all others are using Xe arc-monochromator combination.

ysis difficult). Reaction (3c) and of course its reverse are symmetry-forbidden for the planar configuration of both the ground and first excited states of both *cis*- and *trans*-diimide.

Collisional stabilization of the vibrationally excited ground-state diimide must also be considered. This process is important in the higher azoalkanes, but is negligible in azomethane at atmospheric pressure [4]. It could, however, be important in diimide, despite its molecular simplicity and the consequent short lifetime towards decomposition, because the bond energy for dissociation by reaction (3a) or (3b) is appreciably larger than in azomethane and the energy imparted to it in the present experiments was not greatly in excess of this value. In fact, absolute thresholds for photodissociation by (3a) and (3b) are predicted at 372 and 420 nm respectively. Butane is perhaps the most precise indication of radical formation in the $\text{N}_2\text{H}_2\text{-C}_2\text{H}_4$ photolysis system, and Table 3 shows $\Phi(\text{C}_4\text{H}_{10})$ as a function of wavelength from 325 to 400 nm. There is no trend evident in these data, and no sign of a threshold at 372 nm. This might be taken as evidence for the occurrence of reaction (3b) rather than (3a), but the uncertainty in the measurements at long wavelengths is large because the absorption is weak; there is also considerable uncertainty in the thermochemistry on which the threshold is based, particularly the heat of formation of N_2H . The data also suggest that collisional deactivation of N_2H_2 did not occur, as this should have become less efficient with decreasing wavelength, and an upward trend in $\Phi(\text{C}_4\text{H}_{10})$ should have been observed. On balance, it seems probable that dissociation into radicals via reaction (3a) occurred with a quantum yield of unity, and that the low value of $\Phi(\text{C}_4\text{H}_{10})$ is attributable, as discussed earlier, to chain termination by reactions of N_2H radicals. Reaction (3c), however, although symmetry-forbidden, cannot be ruled out; there is little quantitative information about the energy barriers for symmetry forbidden processes, and it might be competitive with reactions (3a) and (3b), which both have relatively high activation energies.

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