

Di-imide: Some Physical and Chemical Properties, and the Kinetics and Stoichiometry of the Gas-phase Decomposition¹

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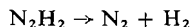
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Preparation of di-imide by passing hydrazine vapor through a microwave discharge yields mixtures with NH_3 containing typically about 15% N_2H_2 , estimated from the gases evolved on decomposition. The behavior of the mixture (which melts at -65°C) on warming from -196 to -30°C suggests a strong interaction between the components. Measurements of magnetic susceptibility and e.p.r. experiments showed that N_2H_2 is not strongly paramagnetic, which with other observations points to a singlet rather than a triplet ground-state.

Di-imide can be vaporized efficiently, together with NH_3 , by rapid warming, and the vapor is surprisingly long-lived, with a typical half-life of several minutes at room temperature. The near-u.v. (3200–4400 Å) absorption spectrum of the vapor was photographed; it shows well-defined but diffuse bands, with $\epsilon_{\text{max}} = 6(\pm 3)$ at 3450 Å.

Di-imide decomposes at room temperature in two ways:



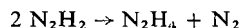
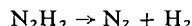
Formation of NH_3 was not observed but cannot be ruled out. The decomposition of the vapor is complicated by a sizeable and variable decomposition that occurs rapidly during the vaporization. The stoichiometry of this and the vapor-phase decomposition depends on total pressure and di-imide concentration. The kinetics of the decomposition of the vapor were studied from 22 to 200°C by following the disappearance of N_2H_2 by absorption of light at 3450 Å, or the formation of N_2H_4 by absorption at 2400 Å, and by mass spectrometry. The kinetics are complex and can be either first- or second-order, or mixed, depending on surface conditions. The effect of olefin additives on the decomposition was studied, and is also complex.

Mechanisms for the decomposition are discussed, including the possible role of *trans-cis* isomerization. The relatively long lifetime found for di-imide in the gas phase suggests that it may be an important intermediate in many reactions of hydronitrogen systems.

La préparation de la di-imide par passage de vapeur d'hydrazine à travers une décharge microonde conduit à des mélanges de NH_3 contenant environ 15% de N_2H_2 , calculés à partir du dégagement gazeux issu de la décomposition. Le comportement de ce mélange (fondant à -65°C) lors du réchauffement de -196 à -30°C laisse penser à une interaction forte entre les constituants. Les mesures de susceptibilité magnétique et les expériences de r.p.e. montrent que N_2H_2 n'est pas fortement paramagnétique ce qui, avec d'autres observations, indique un état fondamental singulet plutôt que triplet.

La di-imide avec NH_3 peut être efficacement volatilisée par un chauffage rapide et la vapeur possède une durée de vie longue (ce qui est surprenant) dont la période type est de plusieurs minutes à la température ambiante. Les spectres d'absorption de la vapeur dans le proche u.v. (3200–4400 Å) ont été photographiés et montrent des bandes bien définies quoique diffuses avec $\epsilon_{\text{max}} = 6(\pm 3)$ à 3450 Å.

La di-imide se décompose à la température ambiante de deux façons



La formation de NH_3 n'a pas été observée mais n'a pas pu être écartée. La décomposition de la vapeur a été compliquée par une autre, notable et variable, qui se produit rapidement lors de la vaporisation. La stoechiométrie de cette dernière et la décomposition en phase vapeur dépendent de la pression totale et de la concentration en di-imide. Les cinétiques de décomposition de la vapeur ont été étudiées de 22 à 200°C en suivant la disparition de N_2H_2 par absorption de la lumière à 3450 Å et par spectrométrie de masse. Les cinétiques sont complexes et peuvent être soit du premier ou du second ordre, ou un mélange des deux dépendant des conditions de la surface. L'effet de l'addition d'oléfin sur la décomposition a été étudié et est également complexe bien qu'une légère réduction ait été observée.

Les mécanismes de la décomposition ont été discutés incluant le rôle possible d'une isomérisation *cis-trans*. La durée de vie relativement longue trouvée pour la di-imide en phase gazeuse laisse penser à son importance en tant qu'intermédiaire dans les nombreuses réactions de systèmes hydroazotés.

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Introduction

Di-imide, $\text{HN}=\text{NH}$, the isoelectronic analog of ethylene and O_2 , and the first member of the azo family of compounds, is of great interest to the chemist. It has generally been thought to be so unstable, however, as to have only a very fleeting existence at room temperature, and our knowledge of it is therefore limited. It appears to be a very active reducing agent in solution in which it can be generated *in situ* by a variety of methods (1), although it has never been detected or isolated in any of these systems. It has been produced and identified spectroscopically in low-temperature matrices (2, 3). It has also been produced and detected in the gas phase in several laboratories. Foner and Hudson (4), in 1958, were the first to detect and identify di-imide, using a mass spectrometer. Di-imide was produced by an electric discharge in hydrazine or hydrazoic acid vapor in a fast-flow system, and was detected downstream from the discharge. They also showed that it could be trapped at -196°C and regenerated in the gas phase on warming. Blau *et al.* (3) obtained the infrared spectrum of the vapor in a similar system. Trombetti studied the absorption spectrum of the vapor in the ultraviolet and the infrared, using a similar flow system (5). These experiments and those of Foner and Hudson indicated a lifetime of at least a second or two for di-imide vapor at room temperature. There is one other brief report in a Ph.D. thesis by Mock at Harvard (6) which suggests a much longer lifetime. Mock generated di-imide vapor by a microwave discharge through hydrazine and by the thermal decomposition of anthracene di-imine, and observed an apparent half-life of a few minutes at low pressure in the inlet manifold of a mass spectrometer, with a measurable signal at $m/e = 30$ persisting for as long as 20 min. Lack of reproducibility and other uncertainties in these experiments led Mock to be understandably cautious in suggesting that di-imide might have a lifetime of this magnitude at room temperature.

With this background, the present work was undertaken to learn more about the chemistry of di-imide vapor, its lifetime, and its mode of decomposition. At an early stage of our experiments it became clear that di-imide was much more stable than generally suspected, and in fact has a lifetime in substantial agreement with Mock's observations. A brief preliminary ac-

count of some of this work has already been published (7).

Experimental and Results

Preparation of Di-imide

Di-imide was prepared by a method similar to those of Foner and Hudson (4), Trombetti, (5), and others, with some modifications. Because we appear to have been able to prepare di-imide in larger amounts and higher concentrations than before, this will be described in some detail.

Anhydrous hydrazine (purity $>99\%$) obtained from Matheson, Coleman and Bell was thoroughly degassed by prolonged pumping with stirring. No attempt was made to dry the hydrazine further, although care was taken not to introduce moisture since water appears to catalyze the decomposition of di-imide. Vigorous stirring of the hydrazine, and a water bath around the reservoir held slightly below room temperature, served to maintain a smooth and adequate flow of vapor. A Teflon-and-glass needle valve controlled the flow rate and pressure of hydrazine vapor. Hydrazine vapor flowed through a quartz tube (13 mm o.d.) in which a microwave discharge was excited with an open-reflector antenna powered by a Raytheon 2450 MHz 100-watt therapy unit. The discharge was initiated by a Tesla coil at a fairly low pressure of hydrazine, giving a hot, intense blue-white discharge which yielded no di-imide. Hydrazine pressure was then increased to the point just before the discharge went out (~ 10 Torr), giving a blueish barely visible discharge with a yellowish core which generated optimum amounts of di-imide. The open-reflector antenna produced more di-imide than did a closed, tuned cavity with better coupling and a more intense discharge. A constriction in the quartz tube just below the discharge improved yields, probably by permitting a higher hydrazine pressure for a given flow rate. Although an apparently feeble, rather cool discharge gave the most di-imide, the yield was nevertheless roughly proportional to the power output of the microwave generator, which was usually set at 100%.

Hydrazine was condensed at -78°C in a U-trap 30 cm below the discharge. This trap was short and wide to minimize blocking and to give rapid passage of gases. A second U-trap further downstream, made of 15 mm o.d. tubing, was cooled in liquid nitrogen, and di-imide con-

densed as a bright yellow solid in a ring starting about 5 mm above the surface of the coolant and extending for several cm. Ammonia condensed with the di-imide but was also spread out through the first arm of the U-trap. The intensity of the yellow color in the trap was a convenient indicator of the efficiency of di-imide production. Noncondensable gases, N_2 and H_2 , were pumped away continuously. Operation of the discharge for 5 min typically produced an estimated 400 μmol of N_2H_2 and about 10 times as much NH_3 in the trap. Considerable amounts of N_2 and H_2 were formed, and about 90% of the original N_2H_4 was recovered in the first trap, so that the yield of N_2H_2 was less than 1% of the hydrazine passed through the discharge.

To transfer di-imide efficiently from the trap at -196°C to the gas phase, it was found essential to vaporize it as rapidly as possible. This was done by quickly raising a beaker of warm water (60 to 70°C) around the trap. Some decomposition always occurred during vaporization, but with this technique di-imide could be vaporized and immediately recondensed in another trap at -196°C with less than 20% loss. Losses were greater with larger samples, probably because gases evolved hindered the distillation. Large samples were therefore prepared by distilling and collecting smaller batches; as much as 0.5 g of di-imide was collected in this way on several occasions. Attempts to remove some of the tenfold excess of ammonia by pumping as it warmed up, or other fractional distillation, met with limited success despite the apparent higher volatility of ammonia (see Fig. 1 and Table 1).

Finally, it is pleasant to report that in none of our experiments with di-imide in the solid, liquid, or vapor phase, at temperatures up to 200°C , was there any sign of explosive behavior. The invariable presence of ammonia as a diluent may be a factor in this observation. Di-imide should undoubtedly be treated with some respect despite its apparent docility, as the decomposition to N_2 and H_2 must be highly exothermic (4).

Properties of Solid and Liquid Mixtures of Di-imide with Ammonia

The solid di-imide trapped with ammonia was stable indefinitely at -196°C , and appeared unchanged on warming to temperatures of about -100°C . On further warming a visible change occurred at about -81°C , when the ring of di-imide appeared to wet the glass surface, be-

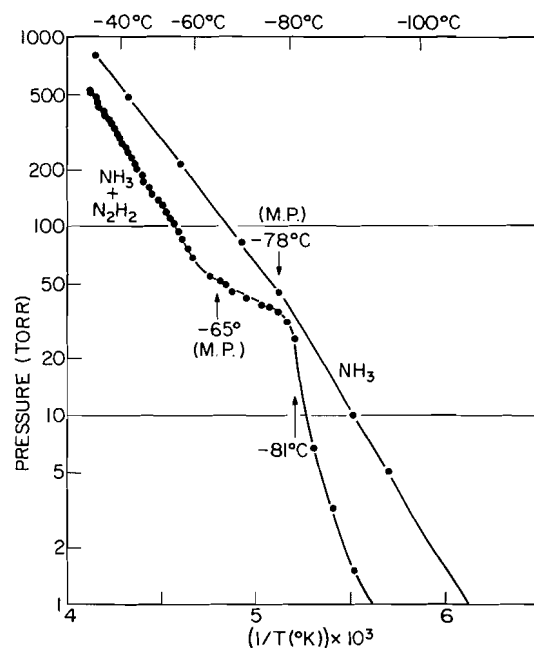


FIG. 1. Van't Hoff plot of ambient pressure over solid and liquid N_2H_2 - NH_3 mixture during slow warming.

came whitish-yellow in color, but remained solid, adhering to the walls of the tube. Nothing further happened until -65°C , when the solid ring melted sharply and ran down to the bottom of the trap as a pale yellow liquid.

The behavior on warming was affected considerably by the ambient pressure. If the trap was open to the pumps or attached to a large evacuated volume, and the liquid nitrogen removed, the mixture at first sublimed away, and on melting bubbled vigorously and boiled away. Little or no di-imide could be recovered from the vapor produced from the liquid mixture, even though the latter retained its yellow color as it boiled away; the decomposition appears to occur somehow during the vaporization process itself. In several experiments the trap was immersed in cold liquid isopentane at about -100°C , and the temperature raised steadily to -30°C over a period of about 30 min. The volume available for evolved gases was about 200 cc and a manometer was attached. Figure 1 shows the pressure as a function of temperature in a Van't Hoff plot ($\log p$ vs. $1/T$ ($^\circ\text{K}$)), and for comparison, the known vapor pressure of ammonia. Several points may be noted. No massive evolution of noncondensable gas (N_2 or H_2) accompanied the

TABLE 1. Yields of di-imide estimated from decomposition products*

Discharge time (min)	Remarks	Products (μmol)					Reaction 1 (%)	H_2/N_2
		N_2	H_2	$\text{N}_2\text{H}_4 + \text{NH}_3$	N_2H_2	N_2H_2 (%)		
3	One trap-to-trap distillation before vaporization	118	18	1529	218 (168)	13.2 (10.5)	8.3 (10.7)	0.16
3	Vaporized directly from U-trap	140	29	1483	251 (196)	15.5 (12.5)	11.5 (14.8)	0.21
1	Vaporized directly from U-trap	67	22	640	112 (90)	15.8 (13.1)	19.6 (24.4)	0.33
2	Vaporized directly from U-trap	114	29	1117	199 (157)	16.2 (13.2)	14.5 (18.5)	0.25
2	Sample pumped on for 40 s after removing liquid N_2 , before vaporizing	71	31	696	111 (91)	14.6 (12.2)	29.0 (34.1)	0.44
10	$\text{N}_2\text{H}_2\text{-NH}_3$ solid sample, scraped from walls of trap as in magnetic susceptibility experiment.	200	45	1257	355 (278)	24.4 (20.1)	12.7 (16.2)	0.22

*Numbers in columns 6, 7, and 8 not in parentheses are based on the assumption that reaction 3 does not occur; numbers in parentheses are based on the alternate extreme assumption that reaction 2 does not occur. Column 7 shows di-imide yield as a percentage of the total condensable gas (N_2H_2 , $\text{NH}_3 + \text{N}_2\text{H}_4$) present in the trap prior to vaporization.

warming; the pressure was always less than the vapor pressure of ammonia. The solid mixture underwent the changes at -81 and -65°C described above with no sharp changes in pressure. At temperatures above -65°C , the liquid was bubbling gently and was probably close to its boiling point from -65 to -30°C . The heating rate was slow enough that self-cooling of the liquid by evaporation should have been minimal, so that the pressure measured in this region was probably close to the saturation vapor pressure of the $\text{NH}_3\text{-N}_2\text{H}_2$ mixture. The fact that this was always much less than that of ammonia means both that N_2H_2 is much less volatile and depresses the vapor pressure of the mixture, and that the two compounds interact strongly to form a very nonideal binary mixture. Recent infrared spectra (8) of $\text{N}_2\text{H}_2\text{-NH}_3$ mixtures in a low-temperature matrix gave evidence for strong hydrogen-bonding, approaching compound formation, on warming from -261 to -240°C , lending support to our present conclusions.

The physical transitions at -81 and -65°C are of interest. Pure NH_3 melts at -78°C , and the first transition might correlate with this melting point, depressed by the N_2H_2 present. Actual melting does not occur, however, and the observed behavior suggests instead formation of a solid solution of NH_3 and N_2H_2 at this point. The ambient pressure falls away from

that of pure NH_3 between -81 and -65°C , perhaps due to a changing composition of the solid solution, while the sharp and invariant melting point at -65°C suggests a eutectic point. The linear Van't Hoff plot above -65°C indicates formation of something like an azeotrope at these temperatures.

The slow warming experiment was repeated but with an atmosphere of nitrogen added at the beginning so that no boiling occurred; excess gases evolved were allowed to vent through the manometer. The same transitions occurred at -81 and -65°C , and there was no visible evolution of gas from the liquid at temperatures up to -25°C . The latter observation and the persistence of the yellow color suggest that di-imide in ammonia solution is fairly stable in this temperature range.

Magnetic Properties of Di-imide

Trombetti has suggested that the ground state of di-imide is a triplet, 3B_g , analogous to the $^3\Sigma_g^-$ state of O_2 . If this is true, di-imide should, like O_2 , be strongly paramagnetic. We therefore examined samples of di-imide, mixed with ammonia as usual, in the solid, liquid, and vapor phases in a Varian E-12 e.p.r. spectrometer.² No absorption was observed in any of the samples.

²We are grateful to Drs. K. F. Preston and J. R. Morton for their cooperation in these experiments.

The solid sample was held at -150°C and the liquid at -60°C . The vapor was studied at room temperature in a flow system with a total pressure of several Torr and an estimated partial pressure of N_2H_2 of at least 50 mTorr. A few mTorr of O_2 gave a large signal under similar conditions.

Because a negative result in a spin resonance experiment is perhaps not conclusive, measurements of the magnetic susceptibility of di-imide were undertaken, using a Gouy balance.³ Two samples were prepared, one by distillation of about 25 mg of the $\text{N}_2\text{H}_2\text{-NH}_3$ mixture from the U-trap and condensation at -196°C in the 3 mm o.d. Pyrex tube used in the susceptibility measurements. The other sample (about 60 mg) was prepared by sealing the sample tube to the bottom of the U-tube and scraping the $\text{N}_2\text{H}_2\text{-NH}_3$ solid from the walls with a magnet sealed in glass, so that it fell into the sample tube as a flaky powder. After filling, both sample tubes were sealed under vacuum and stored at -196°C . Magnetic susceptibility measurements were made with the samples cooled in liquid oxygen in a special Dewar flask.

Both samples showed a very slight paramagnetism after correction for the diamagnetism of the ammonia and the Pyrex tube. Di-imide content was estimated from the gases evolved on decomposition of samples prepared in a similar way (see below). The slight paramagnetism observed was about 1% of that expected if di-imide had the same magnetic susceptibility as O_2 . The source of this weak paramagnetism is not known, and further experiments are planned, but it is clear that solid N_2H_2 at -184°C is not strongly paramagnetic. This observation and the absence of an e.p.r. absorption appear to weigh strongly against a triplet ground state.

The Absorption Spectrum of Di-imide in the Near-u.v.

In addition to the i.r. and vacuum-u.v. spectra which he studied extensively, Trombetti (5) also reported a very weak, apparently continuous absorption centered around 3500 \AA which showed no structure except a slight indication of banding with N_2D_2 . We have confirmed the existence of this absorption, and have been able to examine it in much more detail, probably because we attained much higher pressures of di-

imide than Trombetti. The spectrum was photographed using a Hilger medium-dispersion quartz spectrograph.⁴ A large sample of N_2H_2 and NH_3 was rapidly vaporized into a 7-liter cell, 2 m long, to give a total pressure close to atmospheric and an estimated partial pressure of N_2H_2 of perhaps 50 Torr. Multiple-reflection mirrors gave a light path of 72 m. A strongly banded spectrum was obtained which decayed over a period of a few minutes. Figure 2 shows a densitometer trace from the spectroscopic plate, together with the absorption spectrum of azomethane (9) for comparison. A detailed analysis of the N_2H_2 spectrum will be published elsewhere (10). Spectra taken at higher resolution showed no rotational structure, presumably indicating strong pre-dissociation of the upper state. The absorption by N_2H_2 at 3450 \AA proved to be a very convenient way to monitor its concentration during decomposition (see below).

The Electronic Structure of Di-imide in the Ground-state

Di-imide in a sense lies midway between its isoelectronic analogs, O_2 and C_2H_4 , so that one might expect either a triplet ground-state, like O_2 , or a singlet like C_2H_4 . Another isoelectronic species, HNO , which might be regarded as a

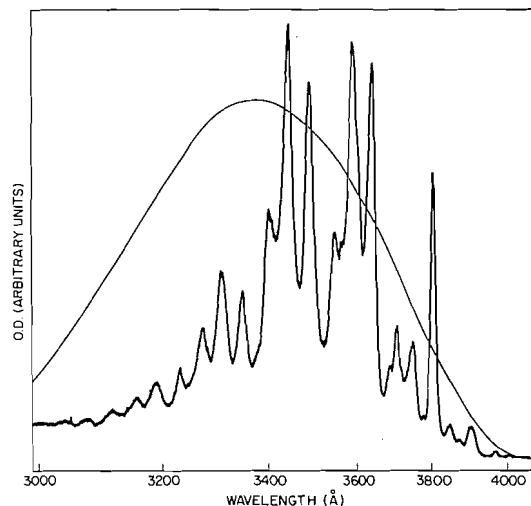


FIG. 2. Densitometer trace from spectrographic plate showing the banded near-u.v. absorption spectrum of N_2H_2 vapor. Also shown is the absorption spectrum of azomethane (8).

³We are grateful to Dr. A. D. Westland of the University of Ottawa for performing the magnetic susceptibility measurements.

⁴We wish to thank Dr. D. A. Ramsay, W. Goetz, M. Barnett, and F. Alberti of these Laboratories for their cooperation in these and later spectroscopic experiments.

"hybrid" of di-imide and O_2 , very probably has a singlet ground-state (11). The nature of the ground-state of N_2H_2 has not yet been clearly established. There now appears to be, however, a substantial body of evidence, including some of our present observations, for a singlet rather than a triplet:

(a) Di-imide showed no appreciable paramagnetism in the gas phase at room temperature, in the liquid at $-60^\circ C$, or in the solid at -184 or $-196^\circ C$.

(b) All other known azo compounds (*i.e.*, substituted di-imides) have singlet ground-states. The near-u.v. spectra of di-imide and azomethane (Fig. 2) are strikingly similar, if one ignores the vibrational structure in the former. Furthermore, we can estimate a decadic extinction coefficient for di-imide at the maximum (3450 \AA) of $6(\pm 3) (\text{cm } M)^{-1}$, close to the value of 4.7 at 3380 \AA for azomethane (9). All other known azo compounds have singlet ground-states, and the near-u.v. absorption is generally agreed to arise from an $n \rightarrow \pi^*$ transition. If di-imide had a triplet ground-state, the near-u.v. transition would be quite different from that of the azoalkanes, and it would seem highly fortuitous that the spectra should be so similar in respect to both λ_{max} and ϵ_{max} .

(c) If the ground-state of N_2H_2 were a triplet, one might expect a weak triplet-singlet absorption analogous to the $^1\Sigma_g^+ \leftarrow ^3\Sigma_g^-$ observed in O_2 near 7650 \AA . A careful search was conducted for absorption in N_2H_2 between 4500 and 9100 \AA , using a 21 ft Eagle spectrograph and path lengths of 80 m , without success. It should be noted that no such absorption at wavelengths longer than that of the near-u.v. $n \rightarrow \pi^*$ transition appears to have been reported for any other azo compound.

(d) A molecular orbital calculation of the energies of the electronic states of *trans*-di-imide predicts a singlet ground-state, with the lowest triplet, formed by an $n_+ \rightarrow \pi^*$ transition, lying some 2.8 eV higher (12). It also suggests that the first excited singlet, also an $n_+ \rightarrow \pi^*$ state, is responsible for the near-u.v. absorption, and predicts an energy of 3.92 eV above the ground-state, corresponding to a wavelength of 3160 \AA . The treatment also predicts several excited singlet states of about the right energy to account for the strong absorption in the vacuum-u.v.

(e) Very recent measurements of the i.r. spectrum of di-imide vapor (13) show an intensity

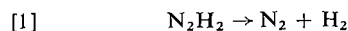
alternation which appears to be unambiguous evidence for a singlet ground-state.

The only evidence for a triplet ground-state is the rotational structure observed by Trombetti (5) in the vacuum-u.v. absorption spectrum, in particular an intensity alternation with the even lines stronger than the odd. This was interpreted as evidence for a ground-state of B_u or B_g electronic symmetry, and from the correlation rules it was concluded that it must be 3B_g , analogous to the $^3\Sigma_g^-$ ground-state of O_2 . There is no obvious alternative to this interpretation. Trombetti's spectrum was obtained using a flow system in which the di-imide passed through the absorption cell within several seconds of its formation in a discharge. This raised the possibility that the spectrum observed was not that of ground-state N_2H_2 , but of a short-lived excited triplet state. We have therefore photographed the vacuum-u.v. spectrum again under similar flow conditions; the flow was then stopped, isolating di-imide in the absorption cell, and spectra were taken at intervals as the di-imide decayed. All spectra obtained were essentially identical to Trombetti's, and decayed slowly over a period of several minutes. The intensity alternation in the rotational structure was confirmed, clearer than before because the spectroscopic light source was more uniform, and there seems no doubt that the spectrum observed in the vacuum-u.v. belongs to the same species of di-imide that we have been studying in the present work.

All things considered, the evidence at the present time strongly suggests that di-imide has a singlet ground-state. It is not clear, however, how the vacuum-u.v. spectrum can be reconciled with this conclusion, and until this conflict has been resolved some doubt must remain.

The Decomposition of Di-imide; Products and Stoichiometry

When di-imide decomposes at room temperature, the only products we have observed are N_2 , H_2 , and N_2H_4 . Ammonia may also be produced (see below) but we have no positive evidence for its formation. The only other hydro-nitrogen compound known to be stable at room temperature is HN_3 , which does not appear to be formed. The decomposition may thus be described, formally at least, as the sum of three reactions





In our initial experiments, measurements of the N_2 and H_2 formed in the decomposition was used to assay the amount of di-imide present. The extent of reaction 1 is measured simply by the yield of H_2 . Analysis of N_2 and H_2 alone cannot distinguish between reactions 2 and 3. The total di-imide decomposed, however, must lie between $\text{H}_2 + 1.5(\text{N}_2 - \text{H}_2)$ and $\text{H}_2 + 2(\text{N}_2 - \text{H}_2)$, the two limits corresponding to the absence of reactions 2 and 3, respectively. Table 1 shows estimates of the di-imide content of a variety of samples estimated in this way. In each case the sample was isolated in a trap at -196°C , thoroughly pumped to remove all volatile gases, vaporized into a suitable closed volume by warming, and the di-imide allowed to decompose at room temperature for 20 min, essentially to complete decomposition. N_2 and H_2 were removed through traps at -196°C by a Toepler pump, measured in a gas burette, and analyzed with a hot Pd thimble. Ammonia present in the traps, together with hydrazine, was vaporized and measured as a gas.

In the first estimate of the rate of decomposition, N_2H_2 was rapidly vaporized, rapidly recondensed at -196°C after a variable time interval, and the noncondensable gases removed for analysis. The remaining N_2H_2 was then allowed to decompose completely, and the gases measured. Di-imide decomposed and di-imide remaining for each decay time was estimated as before from the measurement of N_2 and H_2 . These experiments showed that N_2H_2 vapor decayed with half-life of several minutes. It was also found that even when the di-imide was recondensed within 2 or 3 s of vaporization, a sizeable and variable amount decomposed, never less than about 20%, apparently during the vaporization process itself. It also appeared that the stoichiometry of this decomposition was different from that of the subsequent slow decomposition of the vapor, with relatively more H_2 produced in the latter. To distinguish between the two processes, a sample-splitting technique was required because the decomposition during vaporization was not reproducible. A sample of di-imide was rapidly vaporized simultaneously into two nearly identical 100 ml Pyrex bulbs. Each bulb was then isolated, and in one the di-imide was allowed to decompose completely, while di-imide in the other was rapidly removed and condensed (within 1 or 2 s) at

-196°C . Product gases from the first bulb were those from both the vaporization process and the vapor-phase decomposition, while those from the second were from the vaporization process only. Data obtained in this way are shown in Table 2. The sizeable extent and the irregular variation of the fraction of the N_2H_2 decomposed during vaporization (column 6) may be noted. The ratio of products, H_2/N_2 , was found to vary systematically with the amount of N_2H_2 decomposed, and in a different way for each of the two decomposition processes; this is shown in Fig. 3. For the slow decomposition of the vapor the ratio tends towards unity as the amount of N_2H_2 tends towards zero, and towards zero at high concentration of N_2H_2 . The H_2/N_2 ratio for the decomposition during vaporization is partially complementary, approaching zero at low N_2H_2 concentrations and levelling out at about 0.31 at high.

Estimation of the relative importance of reactions 2 and 3 proved difficult. Colorimetric determination of N_2H_4 (14) produced in the overall decomposition of N_2H_2 always gave values considerably in excess of $\text{N}_2 - \text{H}_2$, an impossible result, probably because of extra N_2H_4 coming from stopcock grease and glass surfaces. A direct spectrophotometric measurement of N_2H_4 in the gas phase seemed more promising. The absorption spectrum of hydrazine vapor above 2000 \AA was measured⁵ and is shown in Fig. 4 together with that of NH_3 (15). Figure 5 shows partial pressure of N_2H_4 measured by light absorption at 2400 \AA (where absorption by ammonia was completely negligible) following rapid vaporization of N_2H_2 (with NH_3) from the U-trap into a 10 cm cylindrical quartz cell mounted in a Heath single-beam spectrophotometer. The figure shows clearly the

⁵The only previous information about the absorption spectrum in this region appears to be in the brief accounts by Imanishi in 1931 and Hilgendorff in 1935 (16). Imanishi reported bands with maxima at 2326, 2320, 2276, 2250, and 2225 \AA , followed by a continuum below 2200 \AA . The only bands we observed, either in the spectrophotometer or in a photographic spectrum taken with a medium-dispersion Hilger spectrograph, correlated with those of NH_3 , an impurity which is difficult to remove completely (these were subtracted from the spectrum shown in Fig. 4). It seems probable that Imanishi's bands had a similar origin, although the wavelengths reported seem to be about 100 \AA units too high. Hilgendorff reported a highly structured spectrum, undoubtedly that of an impurity.

TABLE 2. Products of the decomposition of N_2H_2 during vaporization and after vaporization, using sample-splitting technique*

Total N ₂ H ₂ decomposed (μmol)	Products of decomposition (μmol)				% decomposition during vaporization
	During vaporization		After vaporization		
	H ₂	N ₂	H ₂	N ₂	
1.67	0.031	0.26	0.80	0.99	29
4.40	0.080	0.89	2.20	2.45	39
8.71	0.22	1.44	3.77	4.91	30
11.0	0.54	2.20	3.89	5.53	35
15.9	0.57	4.38	5.17	6.46	51
22.7	1.47	4.59	6.35	10.67	34
30.4	3.06	9.10	4.21	9.74	50
41.3	3.11	11.40	6.06	13.82	48
43.4	3.23	11.13	6.63	15.50	44
56.1	6.98	21.95	4.54	11.86	66
60.2	7.47	23.90	4.89	12.40	67
69.9	5.74	16.47	7.13	24.90	39
78.5	7.60	23.85	5.41	21.92	51
111.8	10.09	31.80	14.12	36.20	48
179.2	16.95	56.70	2.41	42.60	54

*First and sixth columns are based on assumption that reaction 3 does not occur, i.e., N_2H_2 decomposed = $H_2 + 2(N_2 - H_2)$.

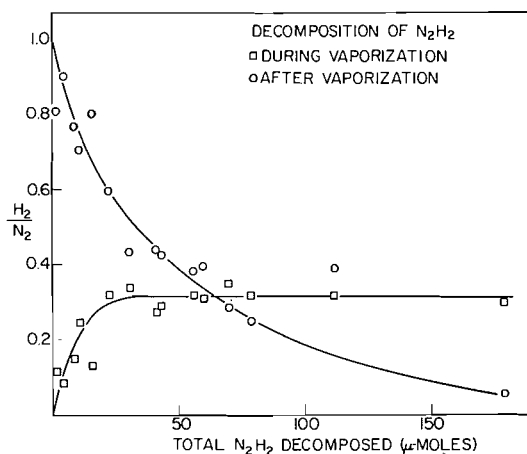


FIG. 3. Product ratios from the decomposition of N_2H_2 , using sample-splitting technique.

N_2H_4 initially present, formed during the rapid vaporization, and then the slow increase, over a period of minutes, as the N_2H_2 decomposed. In a series of experiments, di-imide was vaporized into the spectrophotometer cell and isolated. Initial and final pressures of N_2H_4 were measured as in Fig. 5, and after complete decomposition of the N_2H_2 , N_2 and H_2 were removed from the cell and measured. Results are shown in Table 3, with all quantities expressed as partial

pressures in the reaction cell. Most notable is the large and irregular variation (from 17 to 71%) in the fraction of the total hydrazine present initially, illustrating again the irreproducible character of the decomposition during vaporization. Total product yields were more reproducible; Fig. 6 shows plots of H_2 and N_2H_4 ($\times 2$), which should be equal to the N_2H_2 consumed in reactions 1 and 2, respectively, against total N_2H_2 decomposed. Figure 7 shows a plot of total hydrazine *vs.* $N_2 - H_2$, which should have a slope of one (the straight line in the figure) if reactions 1 and 2 were the only sources of N_2 . Yields of N_2H_4 fell well below $N_2 - H_2$ at the higher pressures, which might be attributed to the occurrence of reaction 3. An equally probable cause, however, is a partial fractionation of the sample during the vaporization from the U-trap, as the less-volatile N_2H_4 would tend to be left behind.

To avoid these problems, a sample-splitting technique was used as before to correct for the N_2 and H_2 formed during vaporization. This permitted comparison of yields of N_2 and H_2 from the vapor-phase decomposition alone with the corresponding yields of N_2H_4 built up during the di-imide decay. From such measurements, hydrazine yields were found, within

TABLE 3. Yields of hydrazine and noncondensable gases from the decomposition of di-imide

Total pressure (Torr)	Total N_2H_4 (Torr)	% of total N_2H_4 present initially	N_2 (Torr)	H_2 (Torr)	Total N_2H_4 decomposed* (Torr)
128	2.27	71	2.56	1.02	4.10
145	1.77	60	2.97	1.15	4.79
216	1.68	36	4.31	1.82	6.80
228	4.34	69	5.52	1.80	9.25
293	4.75	41	9.24	3.75	14.7
301	2.40	39	8.37	4.00	12.7
367	4.23	25	14.2	6.17	22.2
413	3.51	73	5.46	2.61	8.30
471	4.09	54	6.22	2.25	10.2
479	6.17	17	14.4	4.95	23.8
483	7.07	20	22.7	7.90	37.6
522	4.71	48	7.48	2.69	12.3
596	13.27	22	40.9	12.8	68.9
700	9.44	60	23.8	7.49	40.1

*Based on total N_2 and H_2 recovered from reaction vessel after complete decay, assuming $N_2H_4 = H_2 + 2(N_2 - H_2)$. This includes therefore N_2H_4 decomposed during vaporization, the products from which entered the reaction vessel, as well as N_2H_4 which actually entered the reaction vessel as such.

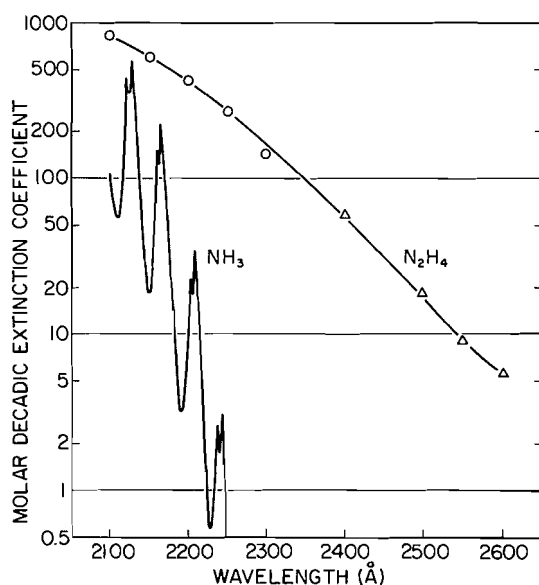


FIG. 4. Absorption spectra of hydrazine and ammonia. O, single measurements with Cary spectrophotometer; Δ , from Beer's Law plots, each with several pressures, using Heath spectrophotometer. Spectrum of ammonia taken from Thompson *et al.* (13).

considerable scatter, to be somewhat in excess of the value of $N_2 - H_2$, suggesting that ammonia formation via reaction 3 was not important in the vapor-phase decomposition.

An attempt was also made to detect ammonia production during the decay of N_2H_4 by fol-

lowing the light absorption simultaneously at two wavelengths, 2192 and 2166 Å, the first at a minimum and the second at a maximum in the NH_3 spectrum (Fig. 4). The increase in optical density during the decay was found to be just proportional to the extinction coefficient of N_2H_4 at each wavelength, implying that only N_2H_4 was produced. The strong absorption by NH_3 initially present made this measurement rather insensitive, however, and permitted only

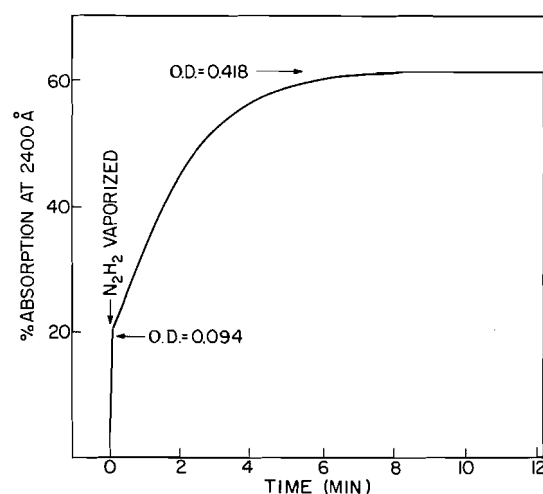


FIG. 5. Absorption at 2400 Å, due to N_2H_4 formed during the decomposition of N_2H_2 .

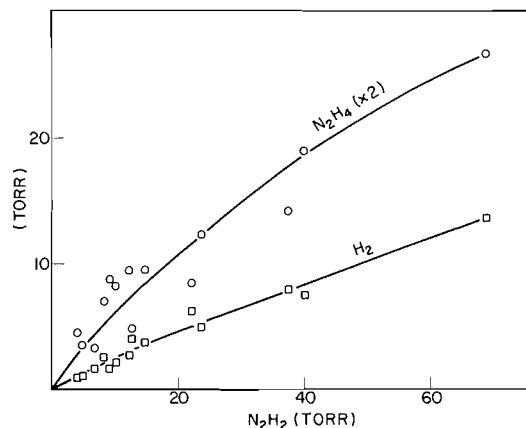


FIG. 6. Yields of H_2 and $N_2H_4(\times 2)$ from the decomposition of N_2H_2 , corresponding to consumption of N_2H_2 in reactions 1 and 2, respectively.

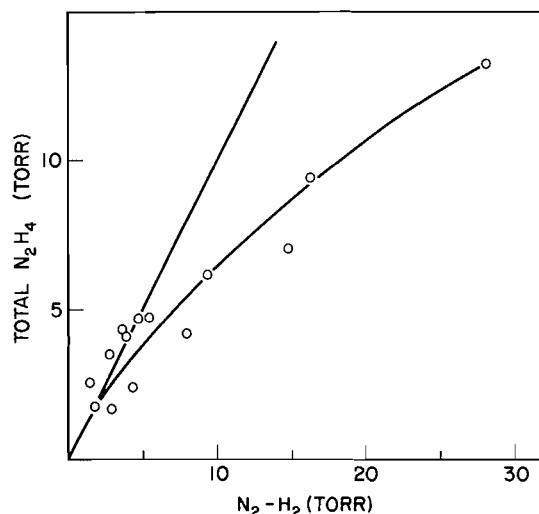


FIG. 7. Yield of N_2H_4 vs. $(N_2 - H_2)$ from the decomposition of N_2H_2 . The straight line corresponds to $N_2H_4 = N_2 - H_2$, the stoichiometry expected if reactions 1 and 2 were the only sources of N_2 .

a rather large upper limit for reaction 3 of 50% of reaction 2.

To sum up, we have no positive evidence for the occurrence of reaction 3, but the large excess of NH_3 always present and the experimental scatter in the product analysis make it difficult to rule out completely.

The Kinetics of the Decomposition of Di-imide

The kinetics of the vapor-phase decomposition was studied directly by following the absorption of light at 3450 \AA in the spectrophotometer cell.

A typical decay curve is shown in Fig. 8, and a first-order plot of the same data in Fig. 9. The decay was also followed by observing the increase in N_2H_4 with time by monitoring the absorption at 2400 \AA , as in Fig. 5. Essentially identical data were obtained from the disappearance of N_2H_2 and the formation of N_2H_4 , indicating a roughly constant stoichiometry throughout the course of the decomposition.

The rate of decomposition appeared to depend on the condition of the surface of the reaction cell. Exposure to air or water vapor always ap-

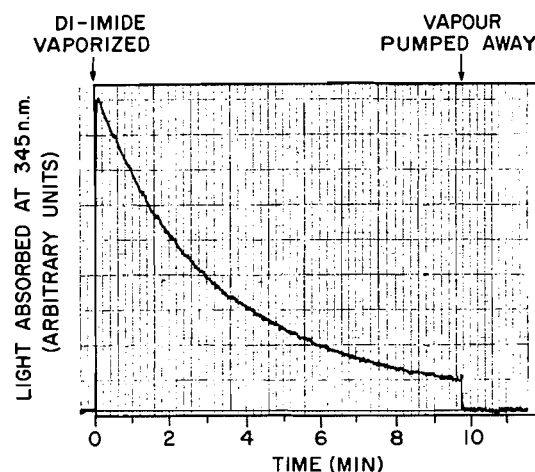


FIG. 8. Disappearance of N_2H_2 in the vapor phase, followed by light absorption at 3450 \AA .

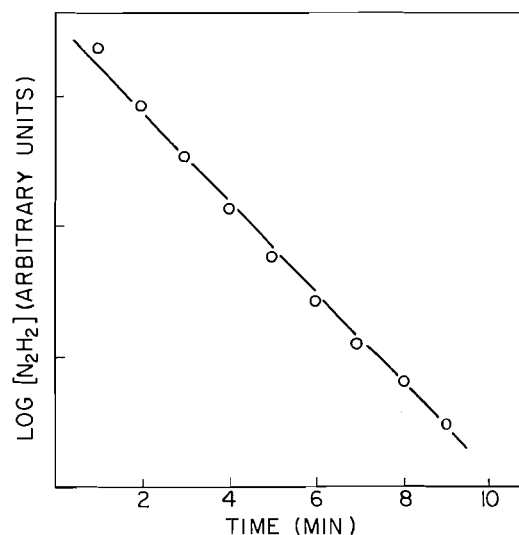


FIG. 9. First-order plot of data from Fig. 8.

preciably increased the rate of decomposition, which subsequently returned to its normal value after prolonged pumping (overnight or longer). The cell was given no special surface treatment, and after prolonged pumping and exposure a few times to the N_2H_2 - NH_3 mixture and its decomposition products, the rate of decomposition became reproducible to about $\pm 10\%$. A dozen experiments, done intermittently over a period of weeks under roughly similar conditions, gave a first-order rate constant of $3.8 (\pm 0.5) \times 10^{-3} \text{ s}^{-1}$ for the disappearance of di-imide at 22°C . In another series of experiments the rate of decomposition was measured with varying amounts of di-imide, corresponding roughly to the conditions of the stoichiometric measurements in Fig. 3. The first-order rate constant showed a steady decrease with increasing amounts of N_2H_2 , approximately parallel to the decrease in H_2/N_2 from the gas-phase reaction. The cell used in these and most of the other experiments was a quartz cell with Suprasil windows, obtained from Hellma (Canada) Ltd. In a similar cell, 20 cm long, made in our glass shop from commercial quartz tubing and Suprasil windows, rates of decomposition were 2 or 3 times faster, and none of a variety of treatments of the surface had much effect. The decay in a Pyrex vessel was

also appreciably faster than in the Hellma cell, which appears to have a surface which is relatively inactive in promoting decomposition of di-imide.

A more striking surface effect was observed following some experiments in which the Hellma cell was exposed to butadiene at 200°C . Subsequently, for several days afterwards, the decomposition of di-imide was markedly slower and showed second-order kinetics. Decay data at 33°C in the butadiene-conditioned cell are shown in Fig. 10. At higher temperatures, mixed first-and-second-order kinetics were observed, tending towards first-order at longer times. The initial second-order rate constant increased with increasing temperature between 30 and 200°C , corresponding roughly to an activation energy of about 20 kcal/mol . The half-life at 200°C , the highest temperature studied, was about 14 s . Over a period of days, with pumping, the cell slowly reverted to its former behavior and di-imide decomposed at about its former rate, generally with simple first-order kinetics. In some experiments an upward curvature was evident in the first-order plot, usually at the beginning of the decay, and examination of earlier data showed that this had occurred in some cases prior to the conditioning by butadiene (Fig. 9, for example, shows distinct curvature). It may be concluded from these experiments that there are (at least) two modes of decomposition of di-imide in the vapor-phase; that the first-order decay in the "normal" cell is surface dependent and was inhibited by conditioning with butadiene at 200°C , and that the slower, second-order reaction only became evident when the first-order process was inhibited or the N_2H_2 concentration was high.

The decomposition of N_2H_2 was also studied briefly by mass spectrometry.⁶ Di-imide (with the usual ammonia) was rapidly vaporized into a tubular Pyrex vessel of about 0.8 l volume to give a total pressure not exceeding a few Torr. A pinhole in a metal disc at one end led to the ionization chamber of an EAI Quad 250A mass spectrometer. Mass spectra were recorded at 10- or 30-s intervals. Signals at $m/e = 1, 2, 28, 31,$ and 32 increased, confirming that $\text{H}_2, \text{N}_2,$ and N_2H_4 were products of the decomposition, while those at 30 and 29 , from N_2H_2 , decreased.

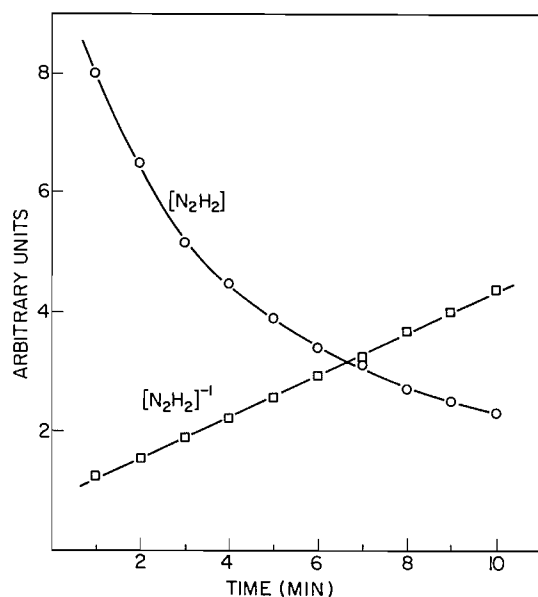


FIG. 10. Plots showing second-order disappearance of N_2H_2 vapor in cell conditioned by butadiene; followed by light absorption at 3450 \AA .

⁶Dr. M. R. Dunn collaborated in these experiments.

Both product formation and di-imide disappearance followed first-order kinetics with a half-life appreciably shorter than that observed in the quartz cell. The faster decay may reflect a more active surface or perhaps the relatively low total pressure and partial pressure of N_2H_2 . Once again, the amount of NH_3 initially present was too large to observe with any accuracy whether or not this was a product of the decomposition.

The Effect of Added Gases on the Decomposition of N_2H_2

Figure 11 shows the effect of several added gases on the product ratio, H_2/N_2 , for gas-phase decomposition of N_2H_2 . The additive was in each case condensed at $-196^\circ C$ with a roughly constant amount of N_2H_2 and NH_3 , and the mixture rapidly vaporized together. Sample splitting was used as before to correct for decomposition during vaporization.

All the additives caused a reduction in the H_2/N_2 ratio. Total product yields were somewhat enhanced, probably because more N_2H_2 was swept into the reaction vessels from the U-trap by the vaporization of the additive. The effect of NH_3 on the H_2/N_2 ratio is significant because NH_3 was present in all our experiments with di-imide. This raises the possibility that the effective variable in Table 2 and Fig. 3 is the pressure of NH_3 rather than the amount of N_2H_2 , since the two were roughly proportional. It appears however that the reduction in H_2/N_2 in the experiments shown in Fig. 3, in which the highest pressure of NH_3 was less than 760 Torr,

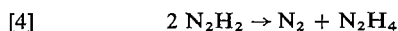
is too large to be explained entirely in this way, although it may be an important factor.

While *n*-butane was somewhat more effective than NH_3 in reducing the H_2/N_2 ratio, the olefins were very much more effective (Fig. 11). This suggests a reaction of the latter with di-imide, so their effect on the rate of disappearance of di-imide was examined. This was complicated by the surface effects noted earlier, but by alternating experiments with and without olefin present, it was possible to conclude that pressures up to 500 Torr of propylene and *cis*-butene-2 had virtually no effect on the rate of decay, but that butadiene definitely enhanced the rate, perhaps by a factor of 2 with 500 Torr at $33^\circ C$. Pressure of NH_3 in these experiments was typically about 200 Torr. Analysis by gas chromatography showed that butene-1 was formed in the reaction with butadiene, but the amounts were small, less than 5% of the N_2H_2 decomposed. The effect of olefins, and particularly of butadiene, on the decomposition of N_2H_2 thus presents some curious contradictions; a strong suppression of H_2 formation in the gas-phase decomposition (Fig. 11), a much lesser effect on the rate of di-imide disappearance, and relatively little formation of reduction products.

Several other gases were tested for their effect on the rate of disappearance of N_2H_2 . Propane, *n*-butane, and nitrogen had no effect at pressures close to atmospheric. Oxygen increased the rate to about the same extent as butadiene.

The Mechanism of the Decomposition of Di-imide

The present study has shown that the decomposition is surprisingly complex, both kinetically and stoichiometrically. The decomposition during vaporization seems most unusual. This is a rapid process, complete in no more than 1 or 2 s. It yields predominately $N_2H_2 + N_2$, but with H_2 becoming important with increasing amount of N_2H_2 (Fig. 3). It does not involve unstable species from the discharge trapped at $-196^\circ C$, because it still occurs after one or more trap-to-trap distillations, each new vaporization causing new decomposition. The major part of this decomposition is perhaps most simply explained by a bimolecular reaction



essentially the same as that occurring more

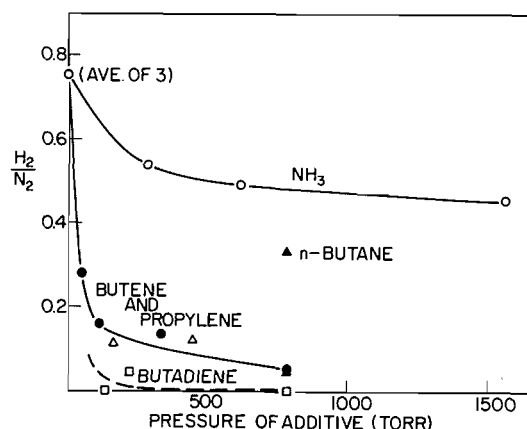


FIG. 11. Effect of additives on the H_2/N_2 ratio from the decomposition of N_2H_2 in the vapor phase.

slowly in the vapor phase, but greatly enhanced by the much higher concentrations present in the transient liquid phase formed during the rapid vaporization of the $\text{NH}_3\text{-N}_2\text{H}_2$ mixture. Formation of H_2 and the increase in the H_2/N_2 ratio with increasing sample size is less easily explained.

There appears to be good evidence for at least two concurrent processes in the decomposition of the vapor. It is reasonable to suggest that reaction 1, occurring largely as a surface reaction, can account for the high value of the H_2/N_2 ratio, approaching unity, at low sample size (Fig. 3); a gas-phase component of this reaction cannot be ruled out. The decrease in H_2/N_2 evident in Figs. 3 and 11 can be explained by reaction 4, occurring as a second-order gas-phase reaction which becomes more important as N_2H_2 concentration increases or reaction 1 is suppressed. The kinetic studies, however, showed that disappearance of N_2H_2 could still be purely first-order under conditions where H_2/N_2 was much less than unity and production of N_2 and N_2H_4 must have been important, which requires that reaction 4 proceed in part by first-order kinetics. One interesting possibility, tentatively suggested by Mock (6) and others, is that the rate-controlling step could be the *trans-cis* isomerization of N_2H_2 , followed by rapid disappearance of *cis*- N_2H_2 via reaction 4 or reaction 1. *cis*-Di-imide has been observed only in the low-temperature matrix-photolysis of HN_3 in which it was presumably formed by reactions of NH radicals (2). It seems fairly well established that only the *trans* form is present in the vapor phase at room temperature and can be trapped downstream from a discharge in hydrazine vapor (5). This suggests that the *cis* isomer is unstable, and certainly *cis* conformation would seem to be required for reactions 1 and 4. Two theoretical treatments of the *cis-trans* isomerism are inconclusive; one indicated that the *cis* isomer is about 8 kcal/mol more stable (thermodynamically) than the *trans*, with a low activation energy (~ 12 kcal) for isomerization (17), while the other predicted just the reverse, the *trans* form more stable and a sizeable barrier (~ 40 kcal) for isomerization (18). *cis*-Di-imide might also be invoked in explaining the decomposition during vaporization. Formation of a certain fraction of *cis* isomer in the liquid phase,

followed by rapid decomposition via reactions 1 and 4, could account for some of the unusual features.

In the present discussion of mechanisms, molecular rather than free-radical reactions have been suggested. Plausible free-radical chains can certainly be written, but the low activation energy, the sizeable reaction rate at room temperature, and the lack of inhibition by olefins make these appear rather unlikely. Reactions forming ammonia have also not been discussed because we have no positive evidence for its formation.

Di-imide as an Intermediate in Other systems

Di-imide has been postulated as a transient intermediate in a variety of gas-phase reactions. These include the combination of NH radicals (19, 20), the reaction of NH with HNCO (21) and with HN_3 (22), and in the photolysis (23), pyrolysis (24), and glow discharge decomposition (25) of N_2H_4 . It has been detected as an intermediate in the decomposition flame of N_2H_4 (26), and in the reaction of O with N_2H_4 (27). In most of these systems di-imide has been regarded as a very short-lived transient that rapidly decomposed, usually to give simply $\text{N}_2 + \text{H}_2$. The relatively long lifetime observed in the present study suggests that di-imide could play a much more complex role in the chemistry of these and other hydronitrogen reaction systems. It might well be a major primary product in processes such as photolysis, pyrolysis, or radiolysis, disappearing by a variety of rapid secondary reactions. The mechanisms of such hydronitrogen systems have remained surprisingly obscure and intractable (the precise mode of formation of N_2 in the photolysis of NH_3 , for example, is not known) and the possible participation of di-imide as a reactive intermediate in some of these systems should be considered.

Di-imide of course has also been postulated as a transient reactive intermediate in aqueous and other solutions in which it is generated *in situ* (1). There seems little doubt that the active reducing agent in these systems is in fact di-imide, although its behavior (rapid and efficient reduction of olefins, or in their absence "self reduction" (reaction 4), with little or no decomposition to N_2 and H_2 (reaction 1)) seems markedly

different than that of di-imide in the present study. The difference presumably must be attributed to solvation effects which greatly enhance the rates of the reduction reactions of di-imide. This might involve facilitation of the *trans*-*cis* isomerization, or preferential formation of the *cis* isomer, since the reduction reactions would seem to require a *cis* configuration. The decomposition of di-imide during vaporization observed in the present work is not unlike the self reduction seen in solution, both in its rapidity and in the preferential decomposition to N_2H_4 and N_2 . This tends to support the suggestion that it occurs in a transient liquid ammonia solution formed during the vaporization process, although the apparent stability of di-imide-ammonia mixtures at temperatures up to $-30^\circ C$ implies a sizeable activation energy if the reaction is to be rapid at the only moderately higher temperatures possible in the vaporizing liquid.

Summary and Conclusions

The present paper describes an investigation of some of the chemistry of "free" di-imide ("free" rather than prepared *in situ* in a reactive medium). The chemistry is obviously complex; more questions have been raised than answered, and much more work is required. Our chief findings may be summarized:

(1) It has been established that di-imide is much more stable than was generally supposed, having a lifetime of minutes at room temperature.

(2) Preparation, techniques of handling, and analysis of di-imide have been studied and described. Some physical properties of di-imide and di-imide-ammonia mixtures have been measured. Measurements of magnetic susceptibility and e.s.r. experiments showed that di-imide is apparently not strongly paramagnetic.

(3) The near-u.v. absorption spectrum of the vapor was measured, and except for a strongly banded structure, was found to be closely similar both in λ_{max} and ϵ_{max} to that of azomethane and other alkyl azo compounds. This, and the lack of paramagnetism suggest that the ground-state of di-imide is a singlet rather than a triplet.

(4) The decomposition of di-imide vapor is complicated by a rapid and sizeable decomposition during vaporization as well as the relatively slow decomposition in the vapor phase. Products

of the decomposition are N_2 , H_2 , N_2H_4 , and possibly NH_3 . Stoichiometry of the two modes of decomposition was different and was affected by sample size, total pressure and presence of added gases.

(5) Kinetics of the decomposition of the vapor was studied spectrophotometrically by following the decrease in light absorption by N_2H_2 at 3450 \AA , or the increase in absorption by N_2H_4 at 2400 \AA . Kinetics were usually approximately first-order, but the decomposition showed a strong surface dependence, and became second-order in a cell conditioned with butadiene. The kinetics are obviously complex, with at least two concurrent processes involved, a decomposition to $N_2 + H_2$, and a bimolecular reaction yielding $N_2 + N_2H_4$, and with reactions occurring both in the gas phase and on the surface. Mechanisms have been tentatively suggested, and the possible role of *cis*-di-imide discussed.

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