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The Photochemistry of N_3^- in Aqueous Solution at 254 mμ

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Irradiation of evacuated aqueous solutions of N_3^- at 254 mμ leads to the production of N_2, NH_2OH, H_2, N_2H_4, and NH_3. At low N_3^- concentration ($\lesssim 10^{-3}$ M) the photolysis has the following stoichiometry: $N_3^- + 2H_2O(h\nu) \rightarrow N_2 + NH_2OH + OH^-$, and the quantum yield is 0.27. The quantum yields of N_2 and NH_2OH depend on the concentration of N_3^- in a way that suggests a competition between N_3^- and H_2O in reacting with the same intermediate. The intermediate is probably the NH radical in its singlet state ($^1\Delta$), produced by the reaction of excited N_3^- with water. NH_2OH is formed by the direct addition of NH to water. The effect of adding NH_3 to the system was tested. The results indicate that NH_3 scavenges the NH radical to form N_2H_4. The rate constants for scavenging of NH by H_2O, NH_3, and N_3^- are in the following ratio: 1:18:285, respectively. The reaction of NH with N_3^- is responsible for the formation of N_2H_4, H_2, NH_3, and further quantities of N_2. The diimide molecule appears to play a prominent role here. The nature of the proposed reactions is discussed.

The photochemistry of N_3^- in solution has been the subject of several works and various mechanisms were proposed.[1-4] However, it appears that all previous works were either fragmentary or involved some experimental errors. Bonnemay[1] reported quantum yields of about 10^4 and proposed a chain reaction mechanism involving excited N_2. Shinohara, et al.,[2] were first misled by his report and postulated excited N_2 and N_3 as chain carriers. Moreover, the system investigated

by these authors was actually the complex $Hg^{2+}N_3^-$; the mercuric ion, which was used as a scavenger, forms a stable 1:1 complex ($K \sim 10^5\ M^{-1}$) which displays an intense absorption band at 248 mμ ($\epsilon_{max} = 4100\ M^{-1}$ cm.$^{-1}$).[5] Thus about 90% of the 254-mμ light was absorbed by this complex in their solutions. The 1.5-mole ratio of yields of N_2 and HgN_3 is thus readily explained.

In previous works, the photolysis was followed by measuring the amounts of OH^{-1} and N_2^2 produced. In his important but rather fragmentary work, Glue[3] reported the formation of H_2, NH_3, N_2H_4, and NH_2OH by the photolysis of 0.2 N NaN_3. To explain the production of NH_2OH, he postulated the generation of NH which reacts with water to produce hydroxylamine: $NH + H_2O \rightarrow NH_2OH$. No evidence was presented to verify his hypothesis. On the other hand, Weiss[4] paid attention to the formation of H_2 and concluded that the primary process involves a charge-transfer-to-solvent (CTTS) type of excitation. This view was also held by Shinohara, et al.[2]

Early works have not been based on a spectroscopic analysis of N_3^-, and in most of them unfiltered light was used for the photolysis. The spectrum of N_3^- was recently investigated[6] and it was shown that the mercury resonance line (254 mμ) lies entirely in the $^1\Delta_u \leftarrow {}^1\Sigma_g^+$ ($\pi^* \leftarrow$ n) band. The corresponding excited state is not dissociative so that its chemical reactivity is primarily due to either interaction with a solvent molecule, a predissociation process, or some kind of preionization process by mixing with the close CTTS state.[6]

This work presents the results of a detailed study of the photochemistry of N_3^- at 254 mμ. The results

(1) M. Bonnemay, J. chim. phys., 41, 18, 56 (1944).
(2) K. Shinohara, T. Shida, and N. Saito, J. Chem. Phys., 37, 2791 (1962); ibid., 39, 1477 (1963).
(3) K. Glue, Ber., 61, 702 (1928).
(4) J. Weiss, Trans. Faraday Soc., 43, 119 (1947).
(5) I. Burak and A. Treinin, unpublished results.
(6) I. Burak and A. Treinin, J. Chem. Phys., 39, 189 (1963).

appear to throw light on some chemical properties of NH and N_2H_2 in solution.

Experimental

Light Sources and Actinometry. A low-pressure mercury arc lamp was used with about 90% of its output at 2537 Å. Longer wave lengths were hardly absorbed by N_3^-. The 1849-Å. line was filtered out by a 5-cm. layer of water contained in a silica cell. Change of light intensity in the range 8×10^{-7}–5×10^{-6} einstein l.$^{-1}$ sec.$^{-1}$ was achieved by varying the position of the lamp with respect to the reaction vessel. Actinometry was carried out by means of the uranyl oxalate actinometer.[7] Total light absorption prevailed in all the experiments where quantum yields were determined.

Reaction vessels were adapted for vacuum photochemical experiments from $1 \times 3 \times 4$ cm. spectrophotometric cells with 3-cm. optical length. The contents of the reaction cell were stirred continuously by a Teflon-coated magnetic stirrer. During irradiation the cell was kept in a thermostated brass compartment in which water at $23 \pm 1°$ was circulated.

Materials. NaN_3 (C.P.) was twice recrystallized from water–ethanol solutions (further recrystallization proved to have no effect on the yields of the photolysis). Triply distilled water was further purified by its exposure to 200-kv. X-rays and then to ultraviolet irradiation overnight to destroy H_2O_2. All other materials used were of Analar grade.

Solutions and Procedure. Deaerated solutions of NaN_3 in water and water–ammonia mixtures were exposed to ultraviolet irradiation. After irradiation, the yields of the following products were determined: N_2, H_2, NH_2OH, N_2H_4, and in few cases NH_3. Owing to experimental difficulties, separate experiments were usually performed to determine the various yields. Thus, for the study of NH_2OH in aqueous solutions, 5×10^{-3} M KH_2PO_4–Na_2HPO_4 buffer (pH 7.3) was used as NH_2OH was found to be somewhat unstable at the basic pH values developed by the photolysis in absence of buffer. On the other hand, no buffer was used for the study of all other products (see Results).

Deaerating the solutions to 1–2×10^{-5} mm. gas pressure was achieved by a brief evacuation followed by stirring the solutions overnight and then another brief evacuation. The concentrated ammonia solutions were frozen during evacuation to avoid considerable evaporation. The pressure of the gas evolved by irradiation was measured as described elsewhere.[8] Mass spectrometric measurements have shown that the gas (which is not condensed in a Dry Ice trap) consists of N_2 with little H_2. The pressure of the H_2 evolved was determined by collecting the gas over a trap of silica gel at liquid air temperature.[9] Since φ_{H_2} was relatively small (less than 10% of the total gas yield), the error involved in its determination might be considerable. Some experiments were designed to check if electrons are primarily released to the solvent during irradiation. For this purpose, the photolysis was

carried out in the presence of few electron scavengers: 10^{-2} M N_2O, 10^{-2} M acetone, and a concentrated phosphate mixture (0.1 M KH_2PO_4 and 0.1 M Na_2HPO_4) + 1 M methanol at pH 6.8. The preparation of the N_2O-containing solutions and the pressure measurements after irradiation were performed as described elsewhere.[8]

The analysis of the irradiated solutions was conducted as follows.

Hydroxylamine was determined by Endres' method[10] modified by using naphthylethylenediamine hydrochloride in place of α-naphthylamine (the former is a better reagent for NO_2^- [11]), and the absorbance was measured at 540 mμ. The N_3^- which seriously interferes with the method was first removed by acidifying the solution with H_2SO_4 in excess, and the HN_3 was then expelled by evaporating the solution under vacuum to about one-fifth of its original volume. The pH of the remaining solution was adjusted to the range 5–6 with sodium acetate–acetic acid buffer and its NH_2OH contents was then determined. The same procedure was employed for the concentrated ammonia solutions; a large excess of $(NH_4)_2SO_4$ does not interfere with the method.

Hydrazine was determined by Watt and Chrisp's method.[12] The azide was first removed as described above, though it does not interfere seriously with the method. To determine N_2H_4 in concentrated ammonia solutions, the excess of NH_3 was removed by evaporation before acidifying the solution with H_2SO_4.

Ammonia. The determination of NH_3 in presence of N_2H_4, NH_2OH, and excess of N_3^- presents a difficult analytical problem. The removal of N_3^- as previously described could not be employed in this case because some of the azide appeared to be thermally converted to ammonia in the strongly acidic solutions. The method used by us is that of Beeghly[13]: NaOH is first added to the sample and the ammonia is separated by steam distillation and determined with Nessler's reagent. NH_2OH, which distills with NH_3, interferes with the method. For this reason, ammonia was determined only in solutions relatively poor in NH_2OH (as that produced from concentrated azide solutions). Correction for NH_2OH (and for N_2H_4 to a smaller extent) was introduced by measuring the color produced in a blank solution containing NH_2OH and N_2H_4 at concentrations which were expected to be produced by the photolysis. Altogether, the determination of NH_3 might involve a relatively large error.

Results

All the quantum yields measured were less than 1. φ_{N_2} was not affected by the presence of N_2O or acetone, and the phosphate–alcohol mixture had no effect on φ_{H_2}. These results seem to rule out mechanisms involving chain reactions or solvated electrons (or H atoms).[14]

(7) E. J. Bowen, "The Chemical Aspects of Light," Oxford University Press, New York, N. Y., 1946.

(8) J. Jortner, M. Ottolenghi, and G. Stein, *J. Phys. Chem.*, **66**, 2037 (1962).

(9) G. Kuhn, *Angew. Chem.*, **44**, 757 (1931). For a recent modification of this method, see U. Sokolov and G. Stein, *Anal. Chem.*, **36**, 1882 (1964).

(10) G. Endres, *Ann.*, **518**, 109 (1935).

(11) F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis," D. Van Nostrand Co., New York, N. Y., 1949, p. 804.

(12) G. W. Watt and J. P. Chrisp, *Anal. Chem.*, **24**, 2006 (1952).

(13) H. F. Beeghly, *Ind. Eng. Chem., Anal. Ed.*, **14**, 137 (1942).

(14) The azide itself may act as an electron scavenger. However, taking into account the rate constants for the scavenging by N_3^- and by the added scavengers (P. Kelly and M. Smith, *J. Chem. Soc.*, 1487 (1961); J. Jortner, *et al., J. Chem. Phys.*, **37**, 2488 (1962); S. Gordon, *et al., Discussions Faraday Soc.*, **36**, 193 (1963)), it appears that the latter

Above pH 7.3 changing the pH had hardly any effect on the yields. Thus, without buffer the pH of the solutions increased from 7 to 11 during irradiations whereas the yields of N_2, H_2, N_2H_4, and NH_3 remained linear with time. Even 3 M KOH had hardly any effect on the yields of H_2 and N_2. The yield of NH_2OH was investigated at various pH values in the region 6.8–8 (attained by a phosphate buffer) and no distinct pH effect was detected. However, the presence of the phosphate buffer had a considerable effect on the yields of N_2H_4 and NH_3. The nature of the effect on $\varphi_{N_2H_4}$ (Figure 1) suggests that the buffer contains some impurities which interfere with the formation of N_2H_4. This view is also supported by the fact that in the presence of H_3BO_3–NaOH buffer, at the same pH and time of irradiation, $\varphi_{N_2H_4}$ was larger. The effect of the phosphate buffer on φ_{NH_3} suggests that the impurities enhance the formation of NH_3. The buffer also led to a small increase of φ_{N_2} ($\lesssim 15\%$).

Figure 2. The effect of N_3^- concentration on the various quantum yields.

Figure 3. The effect of ammonia concentration on the various quantum yields. The concentration of N_3^- is kept constant at 1.3×10^{-2} M.
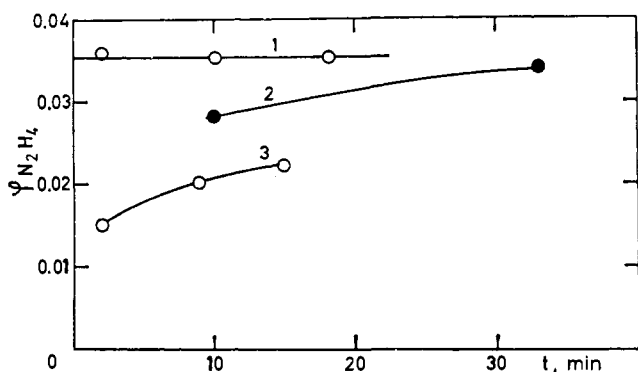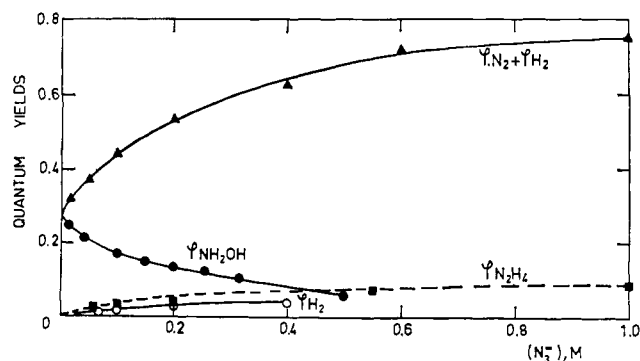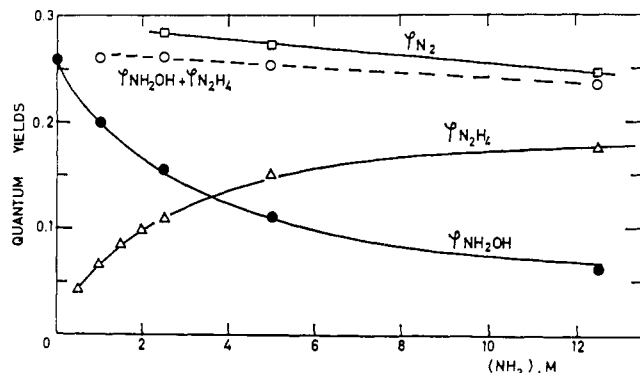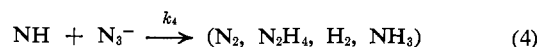

Figure 1. The effect of the phosphate buffer (pH 7.3) on the yield of N_2H_4. The concentrations of N_3^- and buffer are 0.1 and 5 × 10^{-3} M, respectively: curve 1, without buffer; curves 2 and 3, with buffer at light intensities of 4.5 × 10^{-6} and 2.7 × 10^{-6} einstein $l.^{-1}$ sec.$^{-1}$, respectively.

Photolysis of N_3^- in Water. Figure 2 shows the effect of N_3^- concentration on the various quantum yields. At low azide concentration ($\sim 10^{-3}$ M) the photolysis yields N_2 and NH_2OH in equal amounts, this amount being equal to the azide depletion (determined from the lowering of the azide absorbance at 245 mμ which results from the irradiation). Considerable changes are brought about by raising the N_3^- concentration: φ_{NH_2OH} drops down whereas the yields of all other products increase, that of N_2 reaching a value at high N_3^- concentration which is nearly 2.5 times larger than that at low concentration.

Photolysis of N_3^- in Water–Ammonia Solutions. NaN$_3$ (1.3 × 10^{-2} M) was photolyzed in H_2O–NH_3 mixtures of different compositions. The results are shown in Figure 3. There is a striking increase in the yield of N_2H_4 with increasing NH_3 concentration which is accompanied by a decrease in φ_{NH_2OH}. The yield of N_2 is little affected. Hydrogen was not liberated from these solutions. Light intensity had no effect on the quantum yields of the products in water and water–ammonia solutions.

should exert a distinct effect at 0.1 M N_3^-. Some experiments conducted with 10^{-2} M N_3^- also revealed no effect.

Discussion

At low azide concentrations, where $-\varphi_{N_3^-} = \varphi_{N_2} = \varphi_{NH_2OH}$, the photolysis can be summarized as

$$N_3^- + 2H_2O \xrightarrow{h\nu} N_2 + NH_2OH + OH^-$$
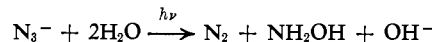
The effect of N_3^- concentration on the yields of the various reaction products (Figure 2) suggests a competition of H_2O and N_3^- on a common precursor which results from the excited azide ion. The reaction of this precursor with H_2O appears to produce NH_2OH, whereas its reaction with N_3^- leads to the formation of N_2H_4, H_2, and NH_3 (and N_2). Since the production of these materials at low concentrations does not affect the production of NH_2OH and conversely (the yields are linear with time), they may be treated independently. We shall first discuss the mechanism of NH_2OH formation as it appears to involve the initial stages of the whole photolysis.

The Origin of NH_2OH. To account for the yield of NH_2OH and its dependence on the N_3^- concentration we propose the following mechanism.

$$N_3^- \underset{}{\overset{h\nu}{\rightleftarrows}} N_3^{-*} \tag{1}$$

$$N_3^{-*} + H_2O \longrightarrow NH + N_2 + OH^- \tag{2}$$

$$NH + H_2O \xrightarrow{k_3} NH_2OH \tag{3}$$

$$NH + N_3^- \xrightarrow{k_4} (N_2, N_2H_4, H_2, NH_3) \tag{4}$$

Reaction 4 represents a set of reactions initiated by the bimolecular interaction of NH with N_3^- (the details of

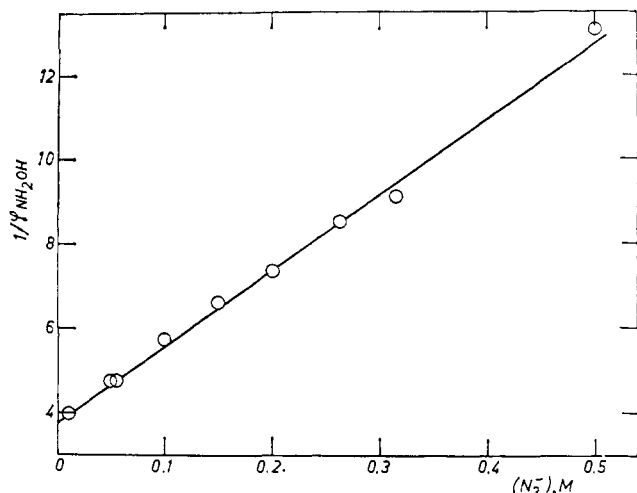Figure 4. The plot of $1/\varphi_{NH_2OH}$ vs. (N_3^-) (test of eq. 5).

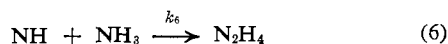Figure 5. The plot of $\varphi_{NH_2OH}/\varphi_{N_2H_4}$ vs. $(H_2O)/(NH_3)$ (test of eq. 7).

this set will be discussed in the next paragraph). Reaction 2 probably proceeds through excited HN_3 as an intermediate.[15] $HN_3^*(^1A'')$ is in a dissociative state so that within 10^{-13}–10^{-14} sec. it will decompose. This time is so short that no reaction is likely to occur between HN_3^* and OH^- even at high alkalinity (this may explain why raising the alkalinity to $3\ M$ KOH has hardly any effect on the yield of N_2). Spin conservation rules require that NH formed by reaction 2 is in a singlet state, probably in the long-lived $^1\Delta$-state (the transition $^1\Delta \rightarrow {}^3\Sigma^-$ is forbidden by both spin and angular momentum selection rules). In this state NH appears to act as a strong Lewis acid, reacting with Lewis bases as H_2O, NH_3, and N_3^-.

The proposed mechanism leads to the relation

$$1/\varphi_{NH_2OH} = 1/\Phi + \frac{(k_4/k_3)(N_3^-)}{\Phi(H_2O)} \tag{5}$$

where φ_{NH_2OH} is the quantum yield of NH_2OH and Φ is the quantum yield of formation of the NH radical (the primary yield of the photolysis). Our results fully confirm this relation (Figure 4). From the intercept of the line we obtain $\Phi = 0.270$, and from the slope, $k_4/k_3 = 285$ (the water concentration was taken to be constant at $55\ M$).

Further evidence to the above mechanism is provided by the experiments with NH_3 solutions. The reaction of NH_3 with NH to form N_2H_4 has been often postulated and experimentally confirmed.[16] Our results suggest that NH_3 competes with other scavengers present in solution on the NH radical. In a system containing $1.2 \times 10^{-2}\ M\ N_3^-$ and a relatively high concentration of NH_3, reaction 4 may be replaced[17] by the reaction

$$NH + NH_3 \xrightarrow{k_6} N_2H_4 \tag{6}$$

Thus, when the reaction of NH with N_3^- may be ignored, the photolysis should yield N_2, NH_2OH, and N_2H_4 (and OH^-). The yield of N_2H_4 should increase with NH_3 concentration in parallel with a reduction in φ_{NH_2OH}, so that $\varphi_{N_2} = \varphi_{N_2H_4} + \varphi_{NH_2OH}$. As to the yield of N_2, it should be equal to ϕ. However, since now the solution is rich with ammonia, ϕ may depend on its concentration. The results shown in Figure 3 generally agree with this interpretation.[18] It appears that ϕ drops with the NH_3 concentration.

From eq. 3 and 6 we obtain

$$\frac{\varphi_{NH_2OH}}{\varphi_{N_2H_4}} = \frac{k_3(H_2O)}{k_6(NH_3)} \tag{7}$$

Figure 5 shows the validity of this relation.[19] From the slope of the straight line we obtain $k_6/k_3 = 18$; i.e., NH_3 scavenges NH 18-fold more effectively than H_2O.

Two more results are in agreement with the proposed mechanism: (a) the yields are independent of light intensity; and (b) small concentrations of impurities, including dissolved oxygen, have no effect on φ_{NH_2OH}. This is readily explained by the reasonable assumption that NH is quickly scavenged by H_2O (or NH_3) which is present in a large excess.

The Origin of N_2H_4, H_2, and NH_3. These products are all formed by the interaction of an intermediate with N_3^-. This is proved by their not being produced by the photolysis of dilute azide solutions ($\lesssim 10^{-3}\ M$). We now turn to discuss the details of the set of reactions represented schematically by reaction 4.

A possible precursor for N_2H_4 is NH_2. However, this possibility is ruled out by the result of carrying out the photolysis in the presence of $1\ M$ ethanol. The latter should scavenge NH_2 and so should lower the yield of N_2H_4 and increase that of NH_3. No such effect was detected. Hence, we propose the following scheme of reactions

$$NH + N_3^- \xrightarrow{k_{4'}\ (+H_2O)} N_2 + N_2H_2 + OH^- \tag{4'}$$

$$NH + N_3^- \xrightarrow{k_{4''}\ (+H_2O)} 2N_2 + H_2 + OH^- \tag{4''}$$

$$2N_2H_2 \xrightarrow{k_8} N_2H_4 + N_2 \tag{8}$$

$$2N_2H_2 \xrightarrow{k_9} HN_3 + NH_3 \tag{9}$$

(15) The A band[6] of N_3^- has $\epsilon_{max} \sim 300$; i.e., the natural lifetime of the excited state is $\sim 10^{-7}$ sec. The reaction of $N_3^-{}^*$ with H_2O may thus compete with deactivation. Another mechanism to be considered is that $N_3^-{}^*$ first undergoes predissociation to yield $N_2 + N^-(^1D)$, the latter then reacting with H_2O.

(16) For a recent review, see R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, **64**, 149 (1964).

(17) In the absence of NH_3 only 6% of the radicals are scavenged by N_3^- at this concentration. In the presence of NH_3, which scavenges NH more effectively than H_2O (see later), the effect of N_3^- is smaller.
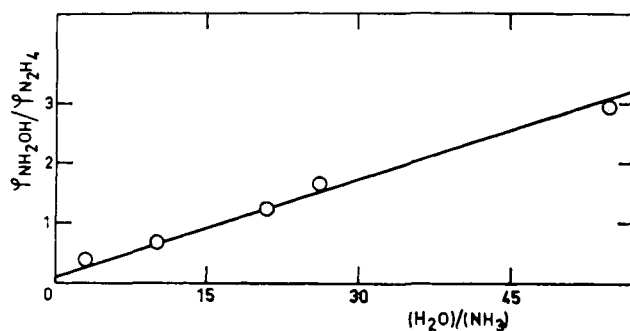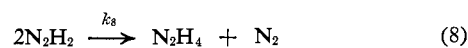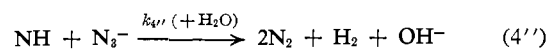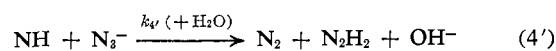
(18) The small discrepancy between φ_{N_2} and the sum $\varphi_{N_2H_4} + \varphi_{NH_2OH}$ is probably due to a systematic error in determining the amount of gas evolved.

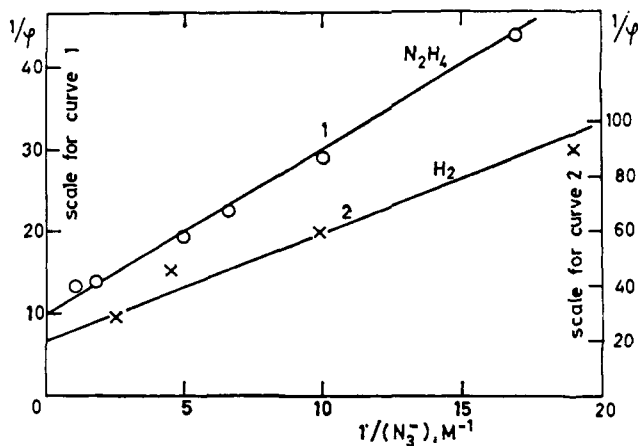(19) Some values of φ_{NH_2OH} were interpolated from the corresponding curve in Figure 3.

Figure 6. The plots of $1/\varphi_{H_2}$ and $1/\varphi_{N_2H_4}$ vs. $1/(N_3^-)$ (test of eq. 11 and 12, respectively).

Figure 7. The plot of the gas yield vs. $(N_3^-)/[(N_3^-) + 0.2]$ (test of eq. 14).

where $k_{4'} + k_{4''} = k_4$. The set thus consists of two pairs of parallel reactions, one involving the NH radicals and the other, the diimide molecules. The reaction $N_2H_2 \rightarrow N_2 + H_2$ is ruled out by the absence of any effect of light intensity on the yields of H_2 and N_2H_4. Such effect should occur if the concurrent reactions involving N_2H_2 are of different orders. Reactions analogous to (4') and (4'') were proposed to occur between NH and HN_3.[16,20,21] N_2H_2 (diimide) was identified in the gaseous products from the electrodeless discharge decomposition of HN_3.[22] Its conversion to N_2H_4 (reaction 8) has been demonstrated.[23] Reaction 9 was also proposed before.[24] Reactions 8 and 9 may proceed through N_4H_4 (tetrazene or isotetrazene) as an intermediate.[22,24]

From eq. 3 and 4 it follows that the fraction of the yield of NH radicals θ reacting with N_3^- is

$$\theta = \frac{(N_3^-)}{(N_3^-) + k_3(H_2O)/k_4} \tag{10}$$

The yield of H_2 is $\theta \Phi k_{4''}/(k_{4'} + k_{4''})$ whereas the yield of formation of diimide is $\theta \Phi k_{4'}/(k_{4'} + k_{4''})$. The material balance yields $\theta \Phi = \varphi_{H_2} + 2\varphi_{N_2H_4} + 2\varphi_{NH_3}$. The yields of ammonia were relatively small and could be determined only at high N_3^- concentration. However, the experimental results reported in Table I appear to be consistent with the predicted material balance.

According to the proposed mechanism the yields of N_2H_4, NH_3, and H_2 should be proportional to θ. Their dependence on the azide concentration can be readily derived from eq. 4', 4'', 8–10. For H_2 and N_2H_4 we obtain

$$1/\varphi_{H_2} = 1/\alpha\Phi + \frac{k_3(H_2O)/k_4}{\alpha\Phi(N_3^-)} \tag{11}$$

$$1/\varphi_{N_2H_4} = 2/\beta\Phi + \frac{2k_3(H_2O)/k_4}{\beta\Phi(N_3^-)} \tag{12}$$

(20) F. D. Rice, Advances in Chemistry Series, No. 36, American Chemical Society, Washington, D. C., 1962, p. 8.
(21) N_4H^- may be formed first by the addition of NH to N_3^-. H. A. Papazian (J. Chem. Phys., 32, 456 (1960)) presented spectroscopic evidence of the formation of N_4H_2 (diiminohydrazine) by the photolysis of solid HN_3 at $-183°$.
(22) S. N. Foner and R. L. Hudson, ibid., 28, 719 (1958); 29, 442 (1958).
(23) E. J. Blau and B. F. Hochheimer, ibid., 41, 1174 (1964).
(24) L. F. Audrieth and B. A. Ogg, "The Chemistry of Hydrazine," John Wiley and Sons, Inc., New York, N. Y., 1951, pp. 119–128.
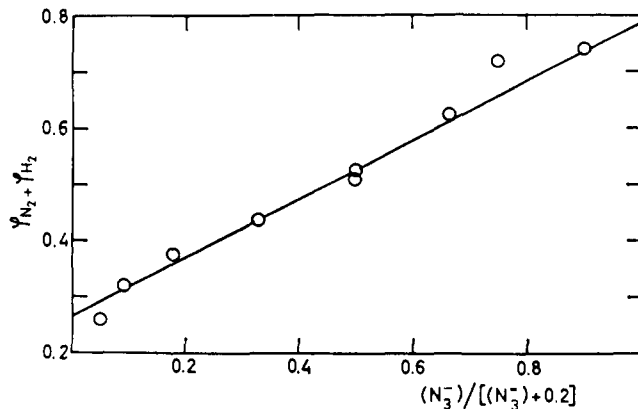
where $\alpha = k_{4''}/k_{4'} + k_{4''}$ and $\beta = (1 - \alpha)k_8/(k_8 + k_9)$. The validity of eq. 11 and 12 is demonstrated in Figure 6. The deviations of φ_{H_2} from the straight line are probably due to experimental errors (see Experimental section). From the N_2H_4 line, we obtain $k_3(H_2O)/k_4 = 0.185$ (i.e., $k_4/k_3 = 300$), $\beta = 0.70$. From the H_2 line, we derive $k_3(H_2O)/k_4 \sim 0.20$, $\alpha \sim 0.18$. The values of k_4/k_3 are in good agreement with those derived from the yields of NH_2OH. From the values of α and β it appears that about 85% of the diimide is converted to N_2H_4 and the rest to ammonia.

Table I

(N_3^-)	$\theta\Phi^a$	$2\varphi_{N_2H_4} + \varphi_{H_2}{}^b$	φ_{NH_3}	$\varphi_{N_2} + \varphi_{H_2}$ Obsd.	$\varphi_{N_2} + \varphi_{H_2}$ Calcd.
0.05	0.054	0.050		0.375	0.364
0.1	0.089	0.087		0.430	0.428
0.2	0.135	0.128		0.525	0.502
0.4	0.180	0.171		0.621	0.550
0.6	0.202	0.191		0.700	0.620
1.0	0.226	0.194		0.725	0.647
2.0	0.254	0.224	0.03	0.775	0.691

^{a} Calculated by means of eq. 10 with $k_3(H_2O)/k_4 = 0.20$. ^{b} Some of the yields were evaluated by interpolation.

The effect of impurities on $\varphi_{N_2H_4}$ and φ_{NH_3} supports the view that these products are formed by a reaction involving two molecules of an unstable intermediate. If the rate constant of the reaction of N_2H_2 with the impurity is not much lower than k_8, the diimide will be effectively scavenged by the impurity. The effectiveness of this process will increase with decrease of light intensity. This conclusion is in complete agreement with the experimental results (Figure 1).

The Yield of Gas. The yield of nitrogen can now be calculated. However, since the *total* pressure of the gas evolved is most readily measured, we shall calculate $\varphi_{N_2} + \varphi_{H_2}$, recalling that φ_{H_2} is $\sim 5\%$ of the total yield of gas. Gas is produced by reactions 2, 4', 4'', and 8 so that

$$\varphi_{gas} = \Phi + \theta\Phi + 2\varphi_{H_2} + \varphi_{N_2H_4} \tag{13}$$

The values of φ_{gas} thus calculated are recorded in Table I (last column). The agreement with the experimental results is satisfactory (see ref. 18).

A general expression for the dependence of φ_{gas} on the azide concentration is obtained from eq. 10–13.

$$\varphi_{gas} = \Phi + \Phi(1 + 2\alpha + \beta/2)\frac{(N_3^-)}{(N_3^-) + k_3(H_2O)/k_4} \quad (14)$$

The validity of eq. 14 with $k_3(H_2O)/k_4 = 0.2$ is demonstrated in Figure 7. From the intercept of the line we obtain $\Phi = 0.265$ which is nearly identical with that derived from the yields of NH_2OH. The value $1 + 2\alpha + \beta/2 = 1.86$ derived from the slope of the line is 9% higher than that directly calculated, using the values of α and β previously determined.

A Simple, Self-Consistent Electrostatic Model for Quantitative Prediction of the Activation Energies of Four-Center Reactions[1]

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The Benson–Bose, semi-ion pair model of the transition state for four-center reactions is extended to include the metathesis reactions, $X_2 + Y_2 \rightleftarrows 2XY$, as well as the addition reactions, $X_2 + olefin \rightarrow product$, and $HX + olefin \rightarrow product$. A simple electrostatic model of point dipoles is used which permits direct calculation of the activation energies of these reactions. These calculated values agree with a large number of experimental data to within ± 1.3 kcal./mole on the average and a maximum deviation of 3.2 kcal./mole. It was found that the best fit could be obtained by using $r_{X-X} + 0.40$ Å. as the transition-state distance for all $X-X$ bonds, where r_{X-X} is the ground-state $X-X$ distance. The dipole–dipole separation is obtained by adding 1.00 Å. to the r_{X-Y} distance, where $X-Y$ is the bond being formed. This leads to a physically reasonable as well as a self-consistent model. Values are given for about 40 reactions involving X, $Y = H$, F, Cl, Br, I. A simple point charge correction is included to account for the Markovnikov rule. Attention is directed to the astonishingly low energies required to produce semi-ion pair states in olefins and the consequences for olefin chemistry.

I. Introduction

The polar character of the transition state of four-center reactions is adequately established by experimental evidence.[2,3] This suggests that the activation process can be described quantitatively by an electrostatic analysis. Benson and Bose[3] performed such an analysis for the addition reaction of hydrogen halides to olefins by using for the transition state an intimate association of two semi-ion pairs. In the present article we describe the extension of this semi-ion pair model to the general family of four-center reactions and describe a simple and consistent scheme for predicting the parameters of the transition state.

In dealing with large intramolecular charge separations, the simplest approach is to assume that a molecule can be approximated by a collection of point dipoles and point aggregates of polarizable matter. This avoids the problem of higher-order interactions (quadrupole, octopole, etc.) which are a consequence of the expansion of the electrostatic potential of the charge distribution in terms of a power series. This simple approach is justified if it gives accurate and consistent results.

II. Physical Model

If the metathesis reactions of $AA^* + BB^* \rightarrow A-B + A^*-B^*$ occurs through a four-center cyclic transition state with partial bonds between all atoms, a reasonable electronic development of the process can be shown as in Figure 1.

In order to pass smoothly from the electronic ground state of the reactants (I) (where there are single bonds A–A and B–B but no bonds A–B) to the electronic ground state of the products (V) (where there are single bonds between the AB's and no A–A or B–B bonds), a concerted polarization of the A–A* and the B–B* bonds in opposite directions must occur (II). This state constitutes an association of two semi-ion pairs (the formal charge on the atoms are $^1/_2$ of the charge of an electron). Energy is required to polarize the single bonds forming the semi-ion pairs. However, part of this electrostatic energy is regained by their mutual interaction in the transition state and it is diminished by the polar energy that might reside in the ground state of the reactants. This charge transfer will continue smoothly through the symmetric state III, with one-electron bonds in all the reaction coordinates. This state is not a transition state in the sense formulated by the transition state theory of chemical reactions. We then find a transition state similiar to II but having the heredity of the products (V). The quantitative equation for predicting the energy of generations of the polar transition state II is

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