sumably being required. This rearrangement evidently involves the transition state of highest energy in the series of steps involved in formation of the various products mentioned.

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DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
LOS ANGELES 24, CALIFORNIA
S. WINSTEIN
M. BATTISTE

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FROZEN NH AND NH_2 RADICALS FROM THE PHOTODECOMPOSITION OF HYDRAZOIC ACID[1]

Sir:

Electronic spectra of NH[2] and NH_2[3] in the gas phase are well known, and recently these fragments, from electrical discharges in NH_3 and N_2H_4, have been trapped and identified in solid rare gases[4,5] at 4.2° K. The gas phase electronic spectrum of N_3 has been identified tentatively.[6] There has been much discussion about these three free radicals as possible intermediates in the photodecomposition of hydrazoic acid in a matrix at low temperature.[7]

We wish to report at this time the results of some preliminary experiments concerning the photodecomposition products of HN_3 trapped in krypton and xenon at 4.2° K. *The electronic absorption spectrum clearly and convincingly demonstrates the presence of NH in considerable amounts and the presence of NH_2 as a secondary reaction product.* The presence of N_3 is suggested tentatively. This is exactly the sequence of products indicated by kinetic studies.[8] A subsidiary mechanism, taking place simultaneously from another part of the potential surface to give H + N_3 directly, cannot be entirely ruled out by these findings since it is at present difficult to estimate the relative concentrations of products in trapped radical experiments. Secondary reactions need not necessarily depend on diffusion of the primary products through the rare gas matrix, because, at the 60:1 mole ratio used, the probability of finding at least one HN_3 molecule as a HN_3 nearest neighbor is 0.18.

Purified Kr or Xe at 1.2 mm. was allowed to leak at the rate of 1.5 ml. (S.T.P.)/min. into the system through a trap containing about 0.1 g. HN_3. The trap was maintained at a temperature of $-108 \pm 2°$, which fixed the mole ratio of rare gas to HN_3 at 60 ± 20. For photolysis, the full arc of a Xe high pressure lamp was used; this gives some intensity down to about 2000 Å. The photolysis was carried out either (I) during the deposition (photodeposition) as in a previous study of diazomethane,[9] or (II) after the HN_3 had been deposited for 6 hours in the dark. Spectra were photographed on a Bausch and Lomb medium quartz spectrograph using, as background source, the high pressure Xe continuum for the ultraviolet and a tungsten filament lamp for the visible.

After 4.5 hours of photolysis in experiment I, the NH absorption appeared with approximately the same intensity as after 2 to 3 hours of photolysis in experiment II. The intensity of NH in II was not dependent on the rare gas used.

The R_{11} (1) lines of the NH (0,0) and (1,0) bands in Kr (see Fig. 1) were found at $\gamma_{\text{vac}} = 29507 \pm 10$ cm.$^{-1}$ and $\gamma_{\text{vac}} = 32460 \pm 15$ cm.$^{-1}$ respectively. The position of the (0,0) band is in excellent agreement with the value 29509 ± 6 cm.$^{-1}$ previously reported[3] for NH in Kr, showing that the trapping site in each case is substantially the same. The broad, high-frequency component of the "doublet" corresponds to the unresolved P and Q branches. Weaker doublets appear 130 cm.$^{-1}$ to the blue, 150 cm.$^{-1}$ and 230 cm.$^{-1}$ to the red of the main doublet, possibly indicating the presence of multiple trapping sites. The details of the fine structure are the same whether the photolysis is carried out by I or II.

It was estimated that, in II after 3 hours, about 20% of the HN_3 had been converted to *trapped* NH. This estimate was made by comparing the integrated intensity of NH with that of benzene under identical deposition conditions, and by taking into account the fact that $f = 0.008$ for the NH transition[10] and $f = 0.0014$ for the 2600 Å. system of benzene.[11] According to the above estimate the solid contains roughly 0.3% of NH. These concentration estimates, however, are based upon a number of uncertainties and should not be taken too seriously.

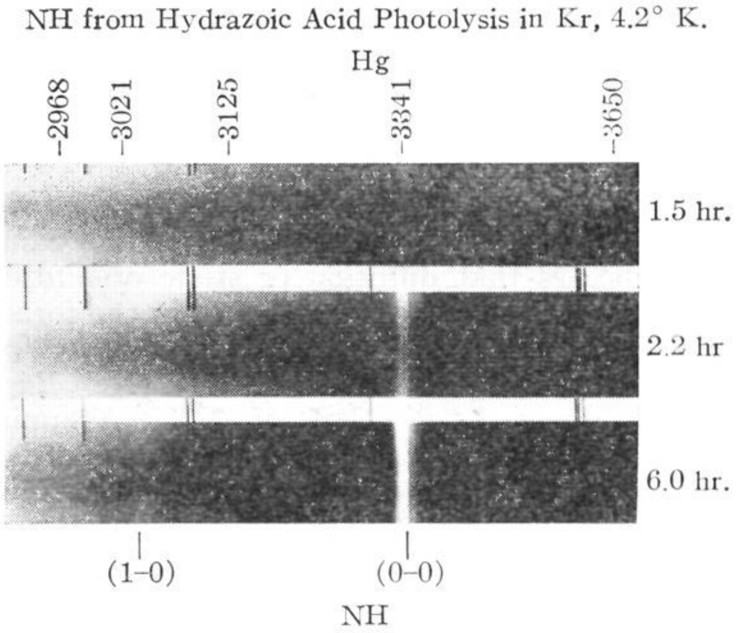

Fig. 1.—NH from the photodecomposition of HN_3 while being deposited in solid Kr at 4.2° K.; photolysis times are on the right.

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[1] Supported in part by the National Science Foundation and the Office of Ordnance Research.

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[8] See, for example, refs. 6 and 7.

[9] M. McCarty, Jr., and G. W. Robinson, THIS JOURNAL, **82**, 1859 (1960).

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The known spectrum[12] of NH_2 in solid rare gas was observed in the visible region. The NH_2 absorption intensity in experiment II after 3 hours of photolysis is approximately five times more intense than it is after 6 hours of photodeposition. In II, the intensity of NH_2 in Kr is roughly twice that in Xe when the photolysis times are the same. This indicates that diffusion or steric orientation effects are important to some extent in the formation of NH_2.

The integrated intensity of NH_2 (Xe, Expt. II) was about 1/200 that of NH. Assuming all the NH_2 to be formed from the reaction of NH with a nearest neighbor HN_3, taking this reaction to be 100% efficient, and using the known oscillator strength of NH, the oscillator strength of the NH_2 ($^2A_1\pi_u$—$^2B_1$) transition is estimated to be 2×10^{-4}. In experiments where free radicals are trapped from electrical discharges[4,5] the intensities of NH and NH_2 spectra are comparable. The presence of weak, broad features in the region near 2600 Å. give rise to the suspicion that the N_3 radical is also trapped in detectable quantities.

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[12] Ref. 4 and unpublished work.

[13] National Science Foundation Predoctoral Fellow.

Contribution No. 2571 from
Leon F. Keyser[13]
Gates and Crellin Laboratories of Chemistry
California Institute of Technology
Pasadena, California G. Wilse Robinson

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TRICHLOROMETHANESULFONYL CHLORIDE AS A SELECTIVE CHLORINATING AGENT[1]

Sir:

Trichloromethanesulfonyl chloride has been found to be an effective free radical chlorinating agent. Specificity in the site of chlorination makes it preferable in certain instances to such chlorinating agents as chlorine and sulfuryl chloride. The reaction can be initiated either photochemically or with benzoyl peroxide. The products of the reaction are equimolecular amounts of the chlorinated substrate, chloroform and sulfur dioxide.

$$Cl_3CSO_2Cl + RH \longrightarrow RCl + HCCl_3 + SO_2$$

The free radical chain sequence shown is suggested to account for these products and their distribution

$$Cl_3C\cdot + RH \longrightarrow HCCl_3 + R\cdot$$

$$R\cdot + Cl_3CSO_2Cl \longrightarrow RCl + Cl_3C\cdot + SO_2$$

In a reaction photo-initiated with a 275-watt General Electric sun lamp, an excess of toluene and 0.10 mole of trichloromethanesulfonyl chloride maintained at 110–115° for eight hours yielded 0.08 mole of sulfur dioxide and 0.08 mole of benzyl chloride (b.p. 79–81° at 25 mm.; n^{25}D 1.5240). In a repetition of this reaction, 0.06 mole of chloroform and 0.06 mole of benzyl chloride were isolated. The infrared spectrum of the benzyl chloride obtained in these reactions was identical with that of an authentic sample. An excess of cyclohexane and 0.20 mole of trichloromethanesulfonyl chloride heated at 80° for 40 hours in the presence of 0.02 mole of benzoyl peroxide resulted in the formation of 0.20 mole of chloroform and 0.20 mole of cyclohexyl chloride (b.p. 140–142° at atm. press., n^{25}D 1.4610). The infrared spectrum of this material was identical with that of an authentic sample of cyclohexyl chloride.

n-Alkylbenzenes are chlorinated only in the benzylic position by this reagent. A reaction mixture consisting of 1.00 mole of ethylbenzene and 0.20 mole of trichloromethanesulfonyl chloride maintained at 78–80° for 72 hours in the presence of 0.012 mole of benzoyl peroxide yielded on distillation 0.11 mole of chloroform and 0.10 mole of α-chloroethylbenzene (b.p. 77–78° at 17 mm.; n^{25}D 1.5230). The infrared spectrum of this chlorinated product showed no absorption band at 718 cm.$^{-1}$, the position at which a very strong absorption band was found to be present in the spectrum of an authentic sample of β-chloroethylbenzene. The infrared spectrum of the chlorination product obtained by the photochlorination of ethylbenzene at this same temperature with chlorine indicated the product to contain about 10% of β-chloroethylbenzene. In a benzoyl peroxide initiated chlorination of ethylbenzene with sulfuryl chloride at 80°, infrared analysis showed that about 7% of the product was the beta isomer.

Trichloromethanesulfonyl chloride also can be used to chlorinate the alkyl side chain of compounds having an aromatically bonded bromine atom without replacement of this bromine by chlorine. Such substitutions are known to occur in chlorinations of *p*-bromotoluene as well as other aryl bromides with both chlorine and sulfuryl chloride.[2] In a photo-initiated reaction, 0.50 mole of *p*-bromotoluene and 0.115 mole of trichloromethanesulfonyl chloride heated at 110–115° for 10 hours gave on distillation 0.10 mole of chloroform and 0.11 mole of *p*-bromobenzyl chloride (m.p. 39–39.5°; reported, 38–39°[3]). There was no evidence of any replacement of the aromatically bonded bromine by chlorine in this reaction.

Selectivity also is noted in the chlorination of *n*-alkanes with this reagent, the hydrogens on a secondary carbon being more susceptible to substitution than hydrogens on a primary carbon. Gas chromatographic analysis[4] of the reaction mixtures obtained in the chlorination of *n*-hexane with chlorine and sulfuryl chloride at 70° indicated the presence of two main mono-chlorinated products. The retention time of the larger chromatographic peak under the conditions specified was 12 minutes and that of the smaller peak, 17 minutes. These retention times were the same as those found for authentic samples of 2-chlorohexane and 1-chlorohexane, respectively.[5] The primary halide amounted to 22% of the mono-chlorinated products in the reaction with chlorine and 17% in the reaction with sulfuryl chloride. However, in both the photo-initiated and benzoyl peroxide initiated reactions of 0.30 mole of *n*-hexane with 0.10 mole of

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[1] Initial experiments performed in The E. C. Britton Research Laboratory, The Dow Chemical Co., Midland, Mich.

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[4] The gas chromatographic analysis were performed on a seven foot, $^1/_4$ inch column packed with 15% di-*sec*-octyl sebacate on Chromosorb W. Column temperature was 78° and the carrier gas was helium with a head pressure of 10 p.s.i.g.

[5] The 2-chlorohexane and 3-chlorohexane were not separated by this chromatographic technique.