

O^{18} via the acid chloride.² The kinetics of the hydrolysis of benzamide in aqueous solutions of hydrochloric acid or sodium hydroxide at $109.0 \pm 0.2^\circ$ were measured by the spectrophotometric determination of the liberated ammonia, using Nessler's reagent.⁴ Labeled benzamide was hydrolyzed under conditions identical to those used in the kinetic determinations. After periods of time corresponding to 0-85% hydrolysis, the reaction was quenched and the unreacted benzamide was isolated (m.p. 127-127.5°). The benzamide samples were pyrolyzed to carbon dioxide⁵ which was analyzed mass spectrometrically.⁶

Oxygen exchange experiments between benzamide- O^{18} (0.58 atom %) and water during basic hydrolysis revealed significant exchange. Benzamide from runs including 21, 25, 28, 37, 55, 75% hydrolysis gave values of 0.33, 0.29, 0.28, 0.24, 0.21, 0.20 atom % O^{18} , respectively. By plotting these data² the ratio of the rate constant of hydrolysis to the rate constant of exchange was evaluated as 0.21. This value should be compared with the value of 4.8 for the k_h/k_{ex} found for the oxygen exchange during ester hydrolysis. The fact that $k_{ex} > k_h$ in the amide hydrolysis, but $k_h > k_{ex}$ in the ester hydrolysis may be related to the competitive breakdown of the addition intermediate $RC(OH)_2X$. The ease of removal of groups is presumably in the order: $OH^- > NH_2^-$ from the amide intermediate and $OR^- > OH^-$ from the ester intermediate. In the amide case the order is in accord with the relative anionic stabilities of the groups, but not in the ester case, in which the large steric requirement of the OR^- group may be important.

However, oxygen exchange experiments between benzamide- O^{18} (0.58 atom %) and water during acid hydrolysis indicated no exchange. Benzamide recovered from runs including 60, 70 and 85% hydrolysis gave values of 0.57, 0.58, 0.58 atom % O^{18} , respectively.⁷ The lack of oxygen exchange in the acid hydrolysis of benzamide may be attributed to the greater basicity of nitrogen relative to oxygen, which results in a displacement reaction without the formation of an addition intermediate.⁸ That the basicity of the nitrogen atom is a factor in determining the course of the hydrolysis is demonstrated by the acid-catalyzed hydrolysis of *p*-benzotoluide- O^{18} (0.98 atom %) in which exchange has been observed (0.93 atom % O^{18} after 25% hydrolysis, $k_h/k_{ex} \sim 5$).

Methyl β -phenylpropionate-carbonyl- O^{18} was prepared from β -phenylpropionic acid.² The kinetics of the α -chymotrypsin catalyzed hydrolysis were followed by titration to constant pH.⁹ After 50%

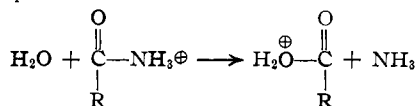
(4) I. Meloche and K. J. Laidler, *THIS JOURNAL*, **73**, 1712 (1951).

(5) W. E. Doering and E. Dorfman, *ibid.*, **75**, 5595 (1953).

(6) A Consolidated-Nier Model 21-201 Isotope-Ratio Mass Spectrometer was used through the courtesy of Dr. H. Taube, University of Chicago under A.E.C. Contract At(11-1)-92.

(7) Private communication from C. A. Bunton, University College, London, confirms the above results qualitatively.

(8) Compare the mechanism in reference 4.



(9) G. W. Schwert, H. Neurath, S. Kaufman and J. E. Snoke, *J. Biol. Chem.*, **172**, 221 (1948).

hydrolysis, the enzyme was precipitated with trichloroacetic acid and the unreacted ester was isolated, distilled, and pyrolyzed to carbon dioxide⁵ which was analyzed mass spectrometrically. The O^{18} content of the unreacted ester and of a blank (excluding enzyme) were identical, indicating no exchange.¹⁰ The lack of oxygen exchange in enzymatic hydrolysis may be attributed to a concerted reaction, to an intermediate involving unsymmetrical oxygens, or to a double displacement involving enzyme.¹¹

Oxygen exchange investigations involving the hydrolysis of acid chlorides, esters, amides, and peptides during acidic, basic and enzymatic hydrolysis are in progress in this laboratory.

(10) S. S. Stein and D. E. Koshland, *Arch. Biochem. Biophys.*, **45**, 467 (1953), reported no oxygen exchange during the hydrolysis of acetylcholine by acetylcholinesterase. D. B. Sprinson and D. Rittenberg, *Nature*, **167**, 484 (1951), and D. G. Doherty and F. J. Vaslow, *THIS JOURNAL*, **74**, 931 (1952), report oxygen exchange between three amino acids (involving the β -phenylpropionyl structure) and water using α -chymotrypsin as catalyst.

(11) M. L. Barnard and K. J. Laidler, *THIS JOURNAL*, **74**, 6099 (1952); D. E. Koshland in W. D. McElroy and B. Glass, "Mechanisms of Enzyme Action," Johns Hopkins University Press, Baltimore, Md., 1954.

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THE YIELDS OF HYDROGEN AND HYDROGEN PEROXIDE IN THE IRRADIATION OF OXYGEN SATURATED WATER WITH COBALT GAMMA-RAYS

Sir:

In the radiation chemistry of water and aqueous solutions, many observations have been interpreted on the basis of the intermediate formation of H , OH , H_2 and H_2O_2 by decomposition of the water. The initial yield of H_2 from oxygen saturated water irradiated with X-rays has been reported¹ to be the same as that from solutions in which the solute prevented secondary reaction of H_2 with OH . This observation was an important consideration in a mechanism proposed² to interpret H_2O_2 formation in oxygen saturated water. Studies of H_2O_2 formation in potassium bromide solutions³ have indicated that this mechanism is not adequate. Previous studies⁴ have indicated that the secondary reaction of H_2 with OH occurs readily, and should lead to a low H_2 yield in oxygen saturated water. The H_2 consumed in this secondary reaction should result in the formation of an equivalent amount of H_2O_2 . We have therefore measured H_2 and H_2O_2 yields from oxygen saturated water in ampoules having no gas space, and also H_2O_2 yields from water through which oxygen was continuously swept during irradiation in order to remove the H_2 produced.

A cobalt-60 γ -ray source giving a dose rate of about 1.7×10^{20} ev./liter-min. was used for these irradiations. All yields are based upon the ferrous sulfate dosimeter with a yield of 15.6 ferrous ions oxidized per 100 ev.

(1) E. R. Johnson and A. O. Allen, *THIS JOURNAL*, **74**, 4147 (1952).

(2) A. O. Allen, *Radiation Research*, **1**, 86 (1953).

(3) T. J. Sworski, *THIS JOURNAL*, in press.

(4) C. J. Hochanadel, *J. Phys. Chem.*, **56**, 587 (1952).

The initial yield of H_2 from oxygen saturated water containing KBr, which prohibits removal of H_2 through secondary reaction with OH, was 0.41 ± 0.01 . The observed initial yield of H_2 from oxygen saturated water was 0.20 ± 0.02 . Thus the H_2 yield was lowered by 0.21 through secondary reaction of H_2 with OH. With oxygen sweeping through the solution during irradiation to remove the H_2 produced, the initial yield of H_2O_2 was 1.10. The initial yield of H_2O_2 in oxygen saturated water in closed vessels was 1.31. Thus, the H_2O_2 formed through secondary reaction of the H_2 was equivalent to the H_2 used up, 0.21. Within experimental error, the initial yields were the same at pH 7 and at pH 2 (H_2SO_4).

These results, combined with results from studies of potassium bromide solutions by Sworski³ indicate that the mechanism proposed by Allen² can be applied to oxygen swept solutions. Our value of 1.10 for the initial H_2O_2 yield corresponds to F + 2E in the Allen terminology, and agrees with the value 1.08 obtained by Sworski by extrapolation to zero potassium bromide concentration. Taking 3.2 as the initial H_2O_2 yield in solutions of hydrogen plus oxygen in which every radical is converted to H_2O_2 ,⁴ the yields of H, OH, H_2 and H_2O_2 from the decomposition of oxygen saturated water by cobalt gamma rays are 2.8, 2.1, 0.41 and 0.76 respectively.

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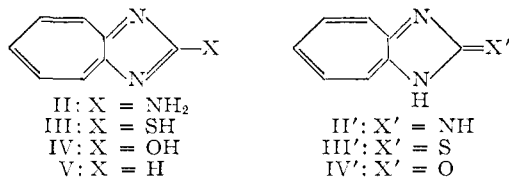
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RECEIVED MAY 10, 1954

1,3-DIAZAZULENE

Sir:

We had previously obtained a compound which was assumed to be 2-amino-1,3-diazazulene (II) or its tautomer (II') by the condensation of tropolone methyl ether (I) and guanidine.¹ 6-Amino-1,3-diazazulene or its tautomer had also been obtained from 2,5-diaminotroponimine and formic acid.² Recently, we obtained 1,3-diazazulene itself and examined its properties. A brief summary of this study is given here.



Reaction of I and one mole equiv. of thiourea in absolute ethanol, in the presence of sodium ethoxide, results in the formation of yellow needles, m.p. 68–70°, in 80% yield. This is a sodium salt and its treatment with acetic acid gives 2-mercapto-1,3-diazazulene (III or III') as orange crystals, m.p. > 300° (Calcd. for $C_8H_6N_2S$: C, 59.19; H, 3.73; N, 17.33. Found: C, 59.52; H, 4.07; N, 17.56). III is sparingly soluble in water and in organic solvents and forms insoluble silver, copper, and iron

(1) T. Nozoe, T. Mukai, K. Takase, I. Murata and K. Matsumoto, *Proc. Japan Acad.*, **29**, 452 (1953).

(2) T. Nozoe, M. Sato, S. Ito, K. Matsui, and T. Matsuda, *ibid.*, **29**, 565 (1953).

salts. Hydrochloride, m.p. > 310° (Found: N, 13.80); picrate, m.p. 262° (dec.) (Found: N, 18.22); methyl thioether (on treatment with diazomethane), m.p. 102° (Found: C, 61.01; H, 4.82; N, 16.67); disulfide, m.p. 218° (dec.) (Found: C, 59.12; H, 3.47; N, 17.42).

Refluxing of III with mercuric oxide in acetic acid or heating of II in a sealed tube at 160–170° with concd. hydrochloric acid, or barium hydroxide results in the formation of 2-hydroxy-1,3-diazazulene (IV or IV') as pale yellow needles, m.p. 245° (Calcd. for $C_8H_6ON_2$: C, 65.75; H, 4.11; N, 19.17; Found: C, 66.14; H, 4.34; N, 18.75). Hydrochloride, m.p. > 300° (Found: N, 15.64); picrate, m.p. 254° (decomp.) (Found: N, 18.56); acetyl compound, m.p. 187° (dec.) (Found: N, 15.26); methylated compound (on treatment with diazomethane), m.p. 186.5° (Found: N, 17.97); 2,4-dinitrophenylhydrazone, m.p. 234° (decomp.) (Found: N, 25.23).

When III is heated on a water-bath for a half hour with 10% nitric acid, it undergoes oxidation and hydrolysis to give 1,3-diazazulene (V) as yellow needles, m.p. 120° (anhydrous, recrystallized from petroleum ether and benzene), in 60% yield. (Calcd. for $C_8H_6N_2$: C, 73.83; H, 4.65; N, 21.54. Found: C, 73.66; H, 4.56; N, 21.58.³ Dipole moment, 4.03 D (25°, benzene) (measured by Mr. Y. Kurita, Nagoya University). V is soluble in water, alcohol, benzene and chloroform. It easily absorbs 1 mole of water of crystallization and gives pale yellow crystals melting at about 60° (Found: C, 64.65; H, 5.44; H_2O , 11.92). Ultraviolet absorption maximum of the hydrate in methanol⁴: 218 $m\mu$ ($\log \epsilon = 4.28$), 250 (4.61), 295 (3.76), 303 (3.78), and 390 (2.97). Infrared absorption maximum of the hydrate in Nujol (5–8 μ region): 6.10 μ (m), 6.27 (m), 7.06 (s), 7.56 (s), and 7.76 (w). V is stable to acids but labile in alkalis. Picrate, m.p. 207° (dec.) (Found: C, 46.95; H, 2.86; N, 19.17); dihydrochloride, darkens at 175° (Found: N, 13.98); methiodide, m.p. 167° (decomp.) (Found: N, 10.68); silver nitrate double compound, m.p. 280° (decomp.) (Found: Ag, 35.27).

Oxidation of V with chromic acid mixture gives imidazole-4,5-dicarboxylic acid,⁵ m.p. 285° (dec.), which is easily decarboxylated to imidazole, m.p. 90°. This fact supports the structures assumed for the above compounds. V does not undergo electrophilic substitution, such as azo coupling, nitrosation, and sulfonation, by the ordinary method. Bromination of V in chloroform gives an insoluble red-colored complex, decomposing at ca. 115°, and yellow crystals, decomposing at ca. 145° (Found: C, 22.10; H, 2.19; N, 6.03). The former contains an active bromine and its reductive decomposition (with potassium iodide followed by sodium thiosulfate) results in the recovery of V. From the ultraviolet absorption spectrum of the yellow crystals (only one max. in methanol at 247 $m\mu$: $\log \epsilon =$

(3) Analyzed sample dried over phosphorus pentoxide in vacuum at room temperature for 48 hours.

(4) The ultraviolet spectral curve in benzene or carbon tetrachloride solution is similar to that of methanol solution but that in cyclohexane is widely different, showing absorption in a longer wave length range than 500 $m\mu$.

(5) H. R. Snyder, R. G. Hendrick and L. A. Brooks, *Org. Syntheses*, **22**, 65 (1942).