were totaled and converted to counts per minute per square yard. These counts, interpreted as total fallout activity, are shown as a function of depth in Fig. 1.

In order to make quantitative estimates of the activities of Cs^{137} and of $ZrNb^{95}$, mock soils were made in the same manner as before, but with known quantities of these isotopes (*6*). Instead of "peeling off" these spectra, the method of Hurley (*7*) was used. Two gamma energy regions were selected, one corresponding to the 0.662-Mev peak of Cs^{137} and the other to the 0.764-Mev peak of $ZrNb^{95}$. These regions permitted good resolution of the two peaks, but contained relatively few counts from the backscatter of other fallout isotopes. From the known spectra of these isotopes, appropriate corrections were made. In no case did they correspond to more than 2 percent of the total counts in question.

In Fig. 2 the distribution in depth of $ZrNb^{95}$ and Cs^{137} is presented. The amount of Cs^{137} below the second inch of soil is about the same for both 1961 and 1962. This indicates that cesium is leached or transported more slowly than $ZrNb^{95}$ and that very little is carried below the fourth inch. The high value for the 1961 0- to 1-inch sample (greater than the 1962 0- to 1-inch sample) could have been caused by a sampling error. Because the transition from the A_0 layer to the top of the soil is often hard to define, it is possible that part of the A_0 layer (which has a higher specific activity) was included in the first inch of soil.

The rise in the concentration of $ZrNb^{95}$ in the fourth inch was quite unexpected. The action of earthworms or other soil organisms in transporting surface organic matter to lower levels in the soil may have contributed to this rise and to the corresponding rise in total fallout activity. Measurements on duplicate samples would, of course, be necessary before general conclusions could be drawn about such effects. However, one may safely conclude (i) that total activity of Cs^{137}, accumulated up to July 1962, was of the order of magnitude of 270 mc/mi^2 for this particular site, and (ii) as a result of the nuclear weapons testing resumed in September 1961, the July 1962 accumulated activity of $ZrNb^{95}$ (due to both Zr and Nb) was approximately 1650 mc/mi^2 (*8*).

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3. Supplied by the Lindsay Chemical Division, American Potash Chemical Corp.
4. Supplied by the New Brunswick Laboratory, U.S. Atomic Energy Commission.
5. Bi^{214} is the principal gamma emitter of the uranium series. Soil samples were counted after being sealed in gas-tight counting cans for at least 2 weeks, thus assuring equilibrium with Ra^{226}. Members of the series above Ra^{226} are low-energy or weak-gamma emitters and thus contribute a negligible amount to the portion of the spectrum with which we are concerned.
6. Supplied by G. J. Karches of the Taft Sanitary Engineering Center, Cincinnati, Ohio.
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8. This work was supported by the National Science Foundation, undergraduate research program grant No. G16300.

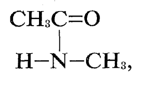
28 September 1962

Catalysis by Imidazole of Deuterium-Hydrogen Exchange in Amide N-H Groups

Abstract. Imidazole, at concentrations of 0.05*M* to 0.2*M*, has been found to increase the rate of deuterium-hydrogen exchange in a model amide by 40-fold or more. Since imidazole side-chains occur in proteins, deuterium exchange in these macromolecules may be strongly affected by the presence of these or similar activating groups.

It has been implicitly assumed in computations based on the rates of deuterium-hydrogen exchange in proteins which contain hydrogen-bonded N-H groups that these groups will exchange deuterium more slowly than will free N-H groups. As one outcome of a recent study of such hydrogen-bonded groups at equilibrium in a model peptide system, it has proved feasible to examine the rates of N-H→N-D exchange in a system with a fixed content of NH···O=C bonded groups. These rates of deuterium-hydrogen exchange have now been found to vary over a range of fortyfold or more with small additions to the solvent, the amounts of which are too small to affect the percentage of N-H groups which are hydrogen-bonded to the carbonyl group.

Exchange rates were followed for N-methylacetamide,



$$\begin{array}{l} CH_3C{=}O \\ \quad\;\, | \\ H{-}N{-}CH_3, \end{array}$$

in dioxane-water mixtures in which, as judged from equilibrium studies, about three-fourths of the amide groups were hydrogen-bonded in molecular aggregates (*1*). All solutions contained 5*M* methylacetamide, and 5*M* D_2O dissolved in dioxane. *p*H was changed by the addition of DCl or NaOD in D_2O. The kinetics were followed from changes in absorbance at 1.42 μ in the near-infrared region of the spectrum.

It was found immediately that the rate of exchange was acid- and base-catalyzed. Such catalysis has already been reported in purely aqueous solutions of N-methylacetamide in which the solute is entirely in the monomeric form (*2*). In our dioxane-water solutions the rates varied only a few percent in the limited *p*H range of about 6.6 to 7.6. To examine the dependence of rate upon ionic strength we also compared the kinetics in 0.01*M* and 0.1*M* tetramethylammonium chloride; the tenfold increase in salt concentration increased the exchange rate by only about 20 percent.

In contrast, additions of imidazole produced striking effects on the velocity of the exchange (Fig. 1). At *p*H 7.4 a tenfold increase in rate was achieved with 0.2*M* imidazole. Even more pronounced catalysis was observed at *p*H 6.7, where the rate constant in the presence of 0.2*M* imidazole was 87 × 10^{-4} liters per mole per minute compared to 2.0 × 10^{-4} in the control (which contained 0.01*M* tetramethylammonium chloride). Exploratory experiments point to even larger effects when the *p*H is lowered further.

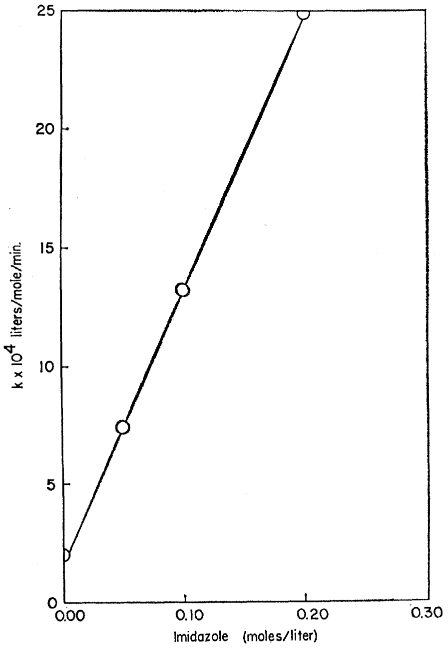


Fig. 1. Rates of deuterium-hydrogen exchange for solutions of D_2O and N-methylacetamide in dioxane, as a function of molarity (*M*) of added imidazole. Temperature, 25°C; *k* is a second order rate constant.

In view of these observations it seems likely that peptide deuterium-hydrogen exchange rates reflect more the state and configuration of acidic and basic side chains in the local environment than the percentage of hydrogen-bonded peptide groups in proteins (3).

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25 September 1962

Schistosoma mansoni: Natural Infection of Cattle in Brazil

Abstract. In an area in Brazil where schistosomiasis has long been endemic, examination of cattle which were slaughtered for food disclosed the presence of adult *Schistosoma mansoni* in the mesenteric veins of four animals. Eggs of *S. mansoni* were found in the feces and rectal mucosa of one animal.

Knowledge of possible animal hosts of a human parasite is important for the control of the infection in endemic areas. Several animal hosts naturally infected with *Schistosoma mansoni* in Africa and South America have been found since 1952. These infections have been reported frequently in South America in small mammals, such as domestic and wild rodents, and the opossum. In Africa, besides rodents, baboons have also recently been found to be infected with *S. mansoni.*

Paulista, State of Pernambuco, a small town near Recife is well known as an important endemic area for schistosomiasis caused by *S. mansoni.* In the abattoir at Paulista, 29 animals, among the cattle killed for food during the months from April to July 1962, were examined and their mesenteric veins were carefully searched for worms. All the animals had been raised in the endemic area. Four animals out of the total at autopsy were infected with adult schistosomes morphologically indistinguishable from *S. mansoni.* Although a thorough search was made no eggs could be found in the feces of three of the infected animals; however, in the fourth infected animal laterally spined eggs were discovered when the mucosa of the animal's rectum was scraped. A total of 67 eggs were seen. All of them had become degenerated and showed a granular interior structure. Eggs were also present in the mucus and in the feces adherent to the mucosa of the animal's rectum. This is the first record of natural infection with *S. mansoni* in cattle. Until the present time no other large quadruped has been found to be a natural host of *S. mansoni.*

The possibility that the schistosome reported here and found in cattle could be a member of the *S. mansoni* complex, an animal instead of a human schistosome, was considered. However, no schistosome species, other than *S. mansoni*, has ever been reported in any mammal in Brazil. The presence of subterminal spines in the eggs of the African species, *Schistosoma rodhaini*, easily distinguishes it from *S. mansoni*, whose eggs have lateral spines.

Although *S. mansoni* could be considered a trematode that lives in several mammals besides man, the significance of the role that animal hosts may play in the maintenance of *S. mansoni* in nature is not understood. (1).

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Atmospheric Photochemical Reactions Inhibited by Iodine

Abstract. The inhibition by iodine of the atmosphere photochemical reaction of olefin with nitrogen dioxide has been confirmed. The presence of iodine in concentrations comparable to those of the reactants retards the formation of aldehyde, peroxyacetyl nitrate, and aerosol as well as the disappearance of olefin. The reaction of iodine with atomic oxygen may account for this inhibition. A number of other potential inhibitors were found to be ineffective.

Photochemical reactions in the atmosphere play a crucial part in the development of several of the symptoms of smog. The oxidation of hydrocarbons initiated by the photolysis of nitrogen dioxide, with the participation of both nitric oxide and nitrogen dioxide, accounts for many of the observed facts, of which one is the formation of ozone. The addition of sulfur dioxide enhances aerosol formation. Free radicals may be involved although there is doubt that chains of any length could develop in the presence of oxides of nitrogen. There have been unpublished reports that molecular iodine inhibits the formation of ozone in systems of irradiated hydrocarbon and nitrogen oxides (1). In addition to possible practical use in controlling atmospheric conditions, inhibition studies may reveal the mechanism of these reactions.

Table 1. Photolysis of cis-2-butene and nitrogen dioxide in air (5 ppm each) with increasing concentrations of iodine.

Iodine (ppm, vol./vol.)	Initial rate of aldehyde formation (ppm/min)
0	0.30
0.22	0.23
0.32	0.075
3.8	0.046
5.6	0.024

Olefins have been found to be the most active of the hydrocarbons. During photolysis of mixtures of olefin and nitrogen oxide at low concentrations in air, the olefin disappears rapidly and yields an approximately stoichiometric amount of a carbonyl compound, along with alkyl nitrate, peroxyacyl nitrate, ozone, and small amounts of other products. The techniques of long-path infrared spectroscopy have proved particularly valuable for the study of these very dilute reactions (2, 3). Accordingly, a short series of experiments were undertaken to investigate the reported inhibition by iodine of atmospheric photochemical reactions.

As a test mixture, concentrations of 5 parts per million (ppm) each of nitrogen dioxide and cis-2-butene in normal air were used. First experiments showed that the formation of the phytotoxic compound peroxyacetyl nitrate was suppressed by the addition of iodine. A further series of experiments showed that the formation of aldehyde was also inhibited.

Instead of dosing the long-path cell with a measured amount of elemental iodine, which is corrosive to many of the metal parts, a few crystals were allowed to vaporize in the circulation system. The amount in the vapor was measured by bubbling a measured volume of the air through potassium iodide solution and estimating the resulting iodine colorimetrically. The values obtained are given in Table 1.

At these concentrations the only cis-2-butene absorption strong enough to measure was the C—H band at 3.4 microns. The products of the reaction collectively absorbed much less at this