A Kinetic Study of the Hydrogen-Bond Dimerization of 2-Pyridone[1]

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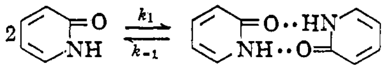
Abstract: Rate and equilibrium constants for the hydrogen-bond dimerization of 2-pyridone in 50 wt % dioxane–carbon tetrachloride, pure dioxane, and 1 wt % water–dioxane have been determined from measurements of ultrasonic attenuation. In the case of the first two solvent systems, activation energies and standard enthalpy and entropy changes were also obtained. The standard enthalpy changes were quite small ($<|-5|$ kcal/mole). In addition standard volume changes accompanying the reaction were estimated from the ultrasonic data. The association rate constant in dioxane (and probably in 1 wt % water–dioxane) has the value characteristic of a diffusion-controlled process ($\sim 10^9\ M^{-1}\ \text{sec}^{-1}$). This is consistent with previous measurements on other hydrogen-bonding systems in relatively inert solvents. The rate constant k_{-1}, which characterizes the dissociation of the dimer, is very sensitive to the solvent, increasing by an estimated factor of 200 in going from benzene to dioxane ($k_{-1} \sim 10^8$ sec^{-1} at 13°) and by an additional factor of 2 when dioxane contains 1 wt % water ($k_{-1} \sim 2 \times 10^8$ sec^{-1} at 13°). This rate constant is a direct measure of the interaction between solvent and 2-pyridone and of the relative thermodynamic stability of the hydrogen bond. These results indicate a considerably greater amount of solvent competition than might be expected on the basis of macroscopic solvent properties (*e.g.*, dielectric constant). In 50 wt % dioxane–carbon tetrachloride, the rate constants cannot be obtained in an unambiguous manner. However, if the association rate is diffusion controlled, the dissociation rate constant has a value intermediate between that found in benzene and dioxane, which is consistent with the hypothesis that this rate constant is a measure of solvent competition for the hydrogen bonds of the solute. The thermal parameters obtained lend support to this interpretation of the data.

The role of the hydrogen bond in biological systems has been the source of considerable speculation and numerous experimental studies.[4,5] However, because of the multiplicity of equilibria competing for hydrogen bonds in biological systems, a quantitative assessment of their net effect on the specific properties of macromolecules is difficult to make. On the other hand, a considerable understanding of the equilibrium properties of simple hydrogen-bonding systems has been obtained, primarily through spectroscopic techniques.[5] Unfortunately, equilibrium studies shed very little light on the mechanism of hydrogen-bond formation and the role of the local environment in determining the properties of hydrogen bonds. Kinetic studies of hydrogen bonding are difficult because of the extreme rapidity of such reactions; however, a few kinetic investigations of hydrogen bonding in "inert" solvents (*e.g.*, CCl_4, benzene, etc.) have been made with ultrasonic and dielectric relaxation techniques.[6,7] More recently, the hydrogen bond has been kinetically implicated in an isomerization of the enzyme ribonuclease,[8] and the possibility of a dynamic role of macromolecular interactions in enzyme catalysis has been suggested.[9] From a biological standpoint, the most interesting type of hydrogen-bonding system is one where the solvent competes with the solute for a hydrogen bond. Very little kinetic information on this problem is available except for ultrasonic studies in systems where an unambiguous interpretation of the results in terms of mechanism and individual rate constants is not possible.[10–12] In principle, kinetic studies of solute hydrogen bonding in water would be the most appropriate model system; however, the equilibrium constants characterizing such systems are quite unfavorable and the reactions are accompanied by essentially no enthalpy or volume changes so that relaxation techniques cannot be employed. Instead we report here the results of a kinetic study of the dimerization of 2-pyridone in *p*-dioxane, 1 wt % water–dioxane, and 50 wt % dioxane–carbon tetrachloride.

2-Pyridone forms a relatively strong hydrogen-bonded dimer according to the equation



(1)

Because of the nature of the dimer formed, further solute polymerization through hydrogen bonding is not possible, and the system can be characterized in a relatively simple fashion. The results obtained indicate that the solvent plays a very crucial role in the dynamics of hydrogen bonding.

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(3) Postdoctoral Fellow of the National Institute of General Medical Sciences, National Institutes of Health (1-F2-GM-5507-01).

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Experimental Section

Materials. 2-Pyridone, obtained from K and K Laboratories, was vacuum sublimed and stored in the dark in a desiccator over phosphorus pentoxide. Solutions were prepared a day or two before use in experiments. *p*-Dioxane (Fisher, AR) was used with no further purification, but fresh bottles were obtained frequently. Karl Fischer titrations indicated less than 0.02 wt % water content in several dioxane samples analyzed. AR carbon tetrachloride was used with no further purification to prepare 50 wt % dioxane-carbon tetrachloride solvent which was stored in a closed vessel with a dry nitrogen atmosphere. Precautions were taken to prevent moisture uptake during preparation of solutions.

Method. The same apparatus and technique as already reported[13] have been used for the present study. Ten or more equally displaced path lengths were used to obtain the pressure amplitude absorption coefficient, α, at each frequency. Measurements were made at approximately 13 frequencies in the range 25 to 150 Mc for each concentration and temperature. Concentrations of 2-pyridone between 0.05 and 0.25 *M* were used. Velocities of ultrasound propagation, v, were also measured by observing on the oscilloscope the time delay in received signal following a change in path length. Separate absorption measurements were made on the solvents at each temperature to ensure that no chemical relaxation of the solvent occurred over the frequency range investigated.

Results and Treatment of Data

In the case where a single relaxation process is observed, the pressure amplitude absorption coefficient, α, may be described by[14,15]

$$\alpha/f^2 = A\tau/(1 + \omega^2\tau^2) + B + \Delta B \qquad (2)$$

where A, B, and ΔB are constants, ω $(=2\pi f)$ is the angular frequency, and τ is the relaxation time. The constant B represents the contribution to α/f^2 of the pure solvent, and ΔB accounts for possible changes in the solvent absorption due to the presence of the solute. Rearrangement of eq 2 into the form

$$1/\Delta \equiv [(\alpha/f^2) - B - \Delta B]^{-1} = 1/A\tau + (\tau/A)\omega^2 \qquad (3)$$

permitted a convenient analysis of the data using $1/\Delta$ and ω^2 as variables. Weighted, least-squares calculations[16,17] were facilitated by an IBM 7094 computer, from which values for A and τ and their standard deviations were obtained. Calculations were cycled through specified increments and ranges of assumed ΔB values. Since an incorrect value of B or ΔB would cause deviations from eq 2, the values of ΔB corresponding to the minimum standard deviations in τ were taken as giving a best fit of the data. In all cases the value of ΔB determined in this manner did not differ significantly from zero.

An alternative analysis of the data can be made when $\Delta B = 0$, by use of the absorption per wavelength due to the chemical reaction, μ_{ch}, which is defined as[14]

$$\mu_{\text{ch}} = 2\alpha_{\text{ch}}v/f \qquad (4)$$

where α_{ch} is the measured absorption coefficient minus the absorption coefficient of pure solvent, and v is the

Table I. Relaxation Times and Maximum Absorptions per Wavelength at Various Pyridone Concentrations

	p-Dioxane													
	13°					25°					40°			
C_0, *M*	0.0508	0.102	0.132	0.162	0.203	0.0514	0.103	0.134	0.164	0.205	0.0522	0.104	0.136	0.208
$10^9\tau$, sec	3.76	2.84	2.45	2.21	2.02	2.96	2.03	1.72	1.05	1.48	1.93	1.42	1.10	1.03
$10^3\ \mu_{\text{m}}$	2.77	4.64	5.92	6.34	7.34	2.50	4.41	6.11	6.22	7.20	2.45	4.21	6.25	7.18

	50 wt. % dioxane-carbon tetrachloride												1 wt. % water-dioxane					
	13°				25°				40°				13°					
C_0, *M*	0.0635	0.122	0.190	0.254	0.0627	0.125	0.188	0.251	0.0617	0.123	0.185	0.247	0.102	0.132	0.162	0.203	0.203	0.254
$10^9\tau$, sec	5.88	4.83	3.53	2.93	4.88	3.31	2.59	2.16	2.40	2.12	1.60	1.34	2.14	1.78	1.63	1.40	1.44	1.24
$10^3\ \mu_{\text{m}}$	2.51	3.86	4.54	5.61	2.53	3.76	4.62	5.53	3.64	4.53	5.64	6.41	3.25	4.13	4.90	5.83	5.81	7.07

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(17) Experimentally the standard deviations, $\sigma(\alpha_i)$, were proportional to the total absorptions, α_i. It may, therefore, be calculated that the weight factors are given to a very close approximation by $W_i = \sigma^2(1/\Delta_1)/\sigma^2(1/\Delta_i) = (\alpha/f^2)_1{}^2\Delta_i{}^4/(\alpha/f^2)_i{}^2\Delta_1{}^4$ where $\sigma(1/\Delta_1)$ is an arbitrary reference standard deviation of $1/\Delta_i$.

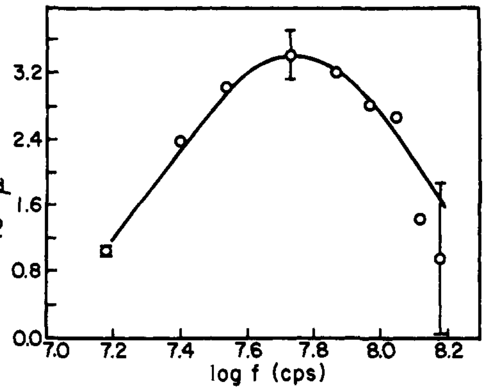

Figure 1. Absorption per wavelength, μ, as a function of frequency, f, for the case of 0.102 M 2-pyridone in p-dioxane at 13°. The line is calculated by use of eq 5. The standard deviations shown correspond to ±2% error in the absorption coefficient, α.

ultrasonic velocity. Rearrangement of eq 2 gives

$$\mu_{\text{ch}} = 2\mu_{\text{m}}\omega\tau/(1 + \omega^2\tau^2) \qquad (5)$$

where the maximum absorption per wavelength, μ_{m}, is equal to $vA/2\pi$. A plot of μ_{ch} *vs.* log f will go through a maximum at $1/\tau = 2\pi f$ so that the relaxation time and maximum absorption per wavelength can be graphically evaluated. An example of such a plot is shown in Figure 1. In all cases the assumption of a single relaxation process was sufficient to describe the data well within experimental error. A summary of the results obtained from analysis of eq 3 is given in Table I.[18]

Assuming the mechanism of hydrogen bonding proceeds according to eq 1, the relaxation time is[14]

$$1/\tau = k_{-1} + 4k_1C_{\text{M}} \qquad (6)$$

where C_{M} is the molarity of monomeric pyridone. Algebraic manipulation of eq 6 gives

$$1/\tau^2 = k_{-1}{}^2 + 8k_1k_{-1}C_0 \qquad (7)$$

where C_0 is the total concentration of 2-pyridone. Plots of $1/\tau^2$ *vs.* C_0 were used to evaluate k_1 and k_{-1} for solutions in pure dioxane solvent as illustrated in Figure 2. In 1 wt % water-dioxane the chemical absorption was quite small so that very high concentrations had to be used (>0.10 M); also the chemical absorption decreases as the temperature is raised so that only one temperature, 13°, was investigated. In this case, the intercept of the $1/\tau^2$ *vs.* C_0 plot was very poorly defined because of the smallness of the intercept and the steepness of the slope. Thus the assumption was made that k_1 was no larger than the value found in pure dioxane, and a minimal value of k_{-1} was calculated from the slope. (This assumption is based on the hypothesis that k_1 in pure dioxane has the value expected for a diffusion-controlled process, which is the maximum possible value for a second-order rate constant; this will be considered further in the Discussion section.)

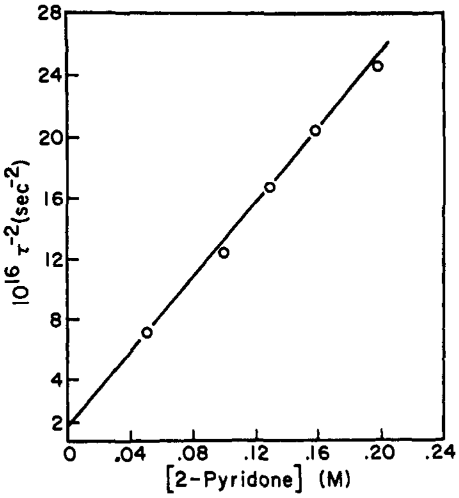

Figure 2. Relaxation time, τ, as a function of the concentration of 2-pyridone in p-dioxane at 13° plotted according to eq 7.

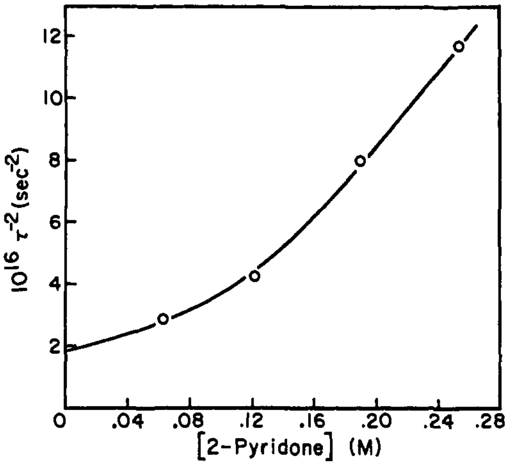

Figure 3. Relaxation time, τ, as a function of the concentration of 2-pyridine in 50 wt % dioxane–carbon tetrachloride at 13° plotted according to eq 7.

When plots of $1/\tau^2$ *vs.* C_0 were constructed for the results obtained in 50 wt % dioxane–carbon tetrachloride, a considerable curvature was visible as shown in Figure 3. Possible explanations for this curvature are as follows: the relaxation process is due to solvent–2-pyridone interactions, the formation of higher polymers than dimers occur, or the activity coefficient of 2-pyridone changes with concentration. The concentration dependence of the relaxation time is incompatible with any reasonably simple mechanism involving solvent–2-pyridone interactions. The formation of polymers cannot be excluded, but it should be noted that only a single relaxation process is observed. The most likely explanation is that the activity coefficient of 2-pyridone changes with concentration. This effect can be formally included in eq 6 and 7,[14] but since the necessary activity coefficients are not known, this would be of no help in analyzing the data. If the association rate is assumed to be diffusion controlled (that is, the rate constant k_1 is identical with that in pure dioxane), values of k_{-1} can be calculated from each measured value of τ by use of eq 7. These rate constants can then be extrapolated to zero concentration, thus eliminating possible effects of polymerization and nonideality. Plots of k_{-1} *vs.* C_0 are reasonably linear and values of k_{-1} obtained by extrapolation are given in Table II together with those for the other solvent systems. The estimated error in the rate constants is ±25 to 50%.

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[18] Analysis of the data by eq 3 cannot distinguish multiple from single relaxation processes in contrast to plots of μ_{ch}. On the other hand, eq 3 provided a more accurate statistical evaluation of the relaxation parameters for our experiments.

Table II. Rate and Equilibrium Constants for Dimerization of 2-Pyridone

Solvent	$10^{-8}k_1$, M^{-1} sec^{-1}	$10^{-8}k_{-1}$, sec^{-1}	k_1/k_{-1}, M^{-1}	Temp, °C
Dioxane	17	0.9	19	13
	21	1.3	16	25
	31	2.2	15	40
	...	...	9.3[a]	30
1 wt % water–dioxane	~ 17[b]	$\geqslant 1.7$[c]	10	13
50 wt % dioxane–CCl$_4$[b]	17	0.14	120	3 1
	21	0.29	73	25
	31	0.46	67	40
Benzene	~ 10[b]	$\sim 3 \times 10^{-3}$ [b]	2720[a]	30

[a] Estimated from molecular weight measurements: M. H. Krackov, C. M. Lee, and H. G. Mautner, *J. Am. Chem. Soc.*, **87**, 892 (1965). [b] Estimated assuming the association rate is diffusion controlled. [c] The equality sign is valid if the association rate is diffusion controlled.

The Arrhenius activation energies were obtained in the usual manner, and standard enthalpy values were calculated from the activation energies. An additional piece of thermodynamic information, the standard volume change for the hydrogen-bonding process, can be obtained from μ_m which can be written as[14]

$$\mu_m = (\rho v^2 \pi C_0 \Gamma / 10^3 RT)[\Delta V^\circ - \beta \Delta H^\circ / \rho c_p]^2 \quad (8)$$

where ρ is the density of the solution, R is the gas constant, β is the coefficient of thermal expansion of the solvent, c_p is the constant pressure specific heat of the solvent, and Γ for the mechanism under consideration is given by[14]

$$\Gamma = (1/8K_aC_0)\{[(1 + 4K_aC_0)/(1 + 8K_aC_0)^{1/2}] - 1\} \quad (9)$$

where K_a is the association constant for the reaction as given in eq 1. The term $\beta\Delta H^\circ/\rho c_p$ is assumed to be negligible relative to ΔV° in the 1 wt % water–dioxane system. The quantity $(\Delta V^\circ - \beta\Delta H^\circ/\rho c_p)$ is assumed to be positive, since the assumption of negative values results in absurdly large values of ΔV° (up to -25 ml/mole). Activation energies, standard enthalpy, and standard entropy changes are given in Table III; average values of the standard volume changes for each solvent and temperature are listed in Table IV. The estimated error in the thermal parameters is ±2 kcal/mole, that in the entropy ± 7 eu, and that in ΔV° ±5 ml/mole.

Table III. Activation and Thermodynamic Parameters for the Dimerization of 2-Pyridone

	Dioxane	50 wt % CCl$_4$–dioxane[a]
E_{a1}, kcal/mole	3.4	3.4
E_{a-1}, kcal/mole	5.1	8.0
ΔH°, kcal/mole	-1.7	-4.6
ΔS°_{298}, eu	0.0	-6.9

[a] Estimated assuming that the association rate is diffusion controlled.

Table IV. Standard Volume Changes for Dimerization of 2-Pyridone

Solvent	ΔV°, ml/mole 13°	25°	40°
Dioxane	11	11	12
1 wt % water–dioxane[a]	12	..	..
50 wt % dioxane–CCl$_4$[a]	5	4	5

[a] Estimated assuming that the association rate is diffusion controlled.

Mention should be made of the fact that measurements were also carried out on pyridone solutions in water, ethanol, toluene, and carbon tetrachloride. Chemical relaxation could not be detected in water and ethanol, while in toluene and carbon tetrachloride the relaxation frequency was too low for measurement with our equipment. Experiments with pyridone solutions in 10 wt % water–dioxane were also unsuccessful because the solvent itself has a relaxation process in the frequency range investigated. This latter system is currently being investigated in detail.

Discussion

An examination of equilibrium constants for solutes in relatively inert solvents[5] (aromatic solvents are probably weak hydrogen-bond acceptors) indicates that pyridone forms one of the most stable hydrogen-bonded dimers known, with the exception of certain zwitterion structures. On the basis of infrared data, Bellamy[19] suggests that this stability arises from a concerted proton-transfer mechanism which provides resonance stabilization to the pyridone dimer. Nevertheless, we see from the results cited in Table II that dioxane reduces the association of pyridone by more than two orders of magnitude from that in benzene solvent, in spite of the fact that the dielectric constant of dioxane (2.209) is actually lower than that of benzene (2.274). The magnitude of the association rate constant in dioxane (and probably in 1 wt % water–dioxane) indicates hydrogen-bond formation is essentially a diffusion-controlled process. Moreover, the associated activation energy, 3.4 kcal/mole, is about what would be expected for a diffusion-controlled process. Thus the relative rate constant for dissociation in these cases is a direct measure of the thermodynamic strength of the hydrogen bond. This correlates well with previous results obtained in inert solvents.[6,7] The dissociation constant increases by at least a factor of 2 when 1 wt % water is added to dioxane. This result is most easily explained if water is assumed to be the dominant solvating species in the immediate vicinity of the pyridone dimer and is also assumed to compete for the pyridone hydrogen bonds much more effectively than dioxane. Thus k_{-1} is a sensitive indicator of specific solvent interactions with pyridone. (The possibility that the relaxation process being observed is a reaction between pyridone and solvent is ruled out by the observed concentration dependence of τ and by the fact that only a single relaxation process is observed.)

If the observed rate of hydrogen-bond formation is essentially diffusion controlled, the actual rate of hydrogen-bond formation between pyridone molecules after they have diffused together must be faster than diffusion apart of the monomers; *i.e.*, the specific rate constant must be greater than 10^9 to 10^{10} sec^{-1}. When 50 wt % dioxane–carbon tetrachloride is the solvent, the

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rate constants are somewhat uncertain because of the previously described treatment of the data. An independent determination of the equilibrium constant would remove this uncertainty. However, the assumption of a diffusion-controlled association is consistent with the few available measurements of such rate constants.[6,7] The dissociation rate constant has a smaller value than found in pure dioxane, its activation energy is larger, and the over-all enthalpy change is more negative. All of these results are quite plausible and are consistent with the idea that the dissociation rate constant is a direct measure of the solvent competition for the hydrogen bonds of the solute.

In all of the solvent systems investigated, the standard enthalpy change is very small, less than $|-2.5|$ kcal/mole of hydrogen bonds. The entropy and volume changes parallel each other, as might be expected.

In summary, specific interactions, rather than macroscopic properties, are responsible for changes in hydrogen-bonding rates and equilibria observed in the various solvents, and kinetic studies provide a tool for probing microscopic solvent structure. In all cases hydrogen-bond formation and dissociation is a rapid process, and hydrogen-bond exchange times are certainly fast enough to permit the most rapid known transformations of polypeptides[13,20] and proteins.[8] Future work will be concerned with investigations of other types of hydrogen bonds.

Acknowledgment. H. O. S. is grateful to Dr. Thomas B. Lewis for helpful instruction on the ultrasonic technique.

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Hydrogen Isotope Effects in the Vapor-Phase Radiolysis of Water

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Abstract: Tritium-labeled water and 1:1 H_2O–D_2O solutions, each containing cyclopentane as additive, were irradiated in the vapor phase by Co^{60} γ rays. Isotopic analyses of the radiolytic hydrogen led to the calculated values of $\alpha_T = 1.7 \pm 0.1$ and $\alpha_D = 1.2 \pm 0.1$ as the relative rates for H *vs.* T and H *vs.* D atom formations. These values are much smaller than the values of 2–6 reported for the deuterium isotope effect in the radiolysis of liquid water, indicating that different reaction processes are involved.

Although differences in zero-point energies between hydrogen isotopes (protium, deuterium, and tritium) seem negligibly small relative to the high energies available in radiation-induced reactions, significant isotope effects are often observed. The values reported for "molecular" hydrogen and hydrogen-atom formations,[1-3] as well as those observed for hydrogen abstraction by hydrogen atom and other radical intermediates,[4,5] are surprisingly large.

In the radiolysis of water and dilute aqueous solutions, where the reaction processes are reasonably well established,[6] numerous estimates of isotope effects for both "molecular" hydrogen and hydrogen-atom formations have been made.[1-3] There estimated values are highly sensitive to possible effects of added solutes on the rather complex series of reaction processes. Isotope effects are found to be somewhat different in acid and neutral solutions, and the hydrogen relative to deuterium-enrichment values (α_D) for both "molecular" hydrogen and hydrogen-atom formations varied between 2 and 6.

Recent investigations[7-10] have demonstrated that in the radiolysis of water vapor, a relatively simple set of reaction processes is involved. In the absence of tracer impurities, back reactions of hydrogen atoms and hydroxyl radicals take place effectively, and very little products are observed. In the presence of organic additives, these intermediates undergo hydrogen-abstraction reactions to give large yields of hydrogen. From a study of the hydrogen isotopic composition relative to that in the reactant water, we have calculated isotope effects for the hydrogen-atom formation.

Experimental Section

Materials. Cyclopentane and cyclohexane were Phillips research grade products, and were further purified by slow passage through 2-ft silica gel columns to remove unsaturated hydrocarbon contaminants. Phillips research grade ethylene was purchased from the Matheson Co., and it was used without purification except for the usual degassing at 77°K. Deuterium oxide was purchased from the Oak Ridge National Laboratory and tritium-labeled water from the New England Nuclear Corp. Both the deuterated and the tritiated water samples were treated by Co^{60} γ irradiation, followed by degassing and photolysis with long-wavelength ultraviolet light.[11] Ordinary water was purified by the usual procedure

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