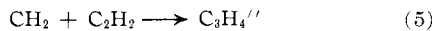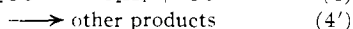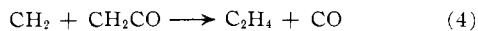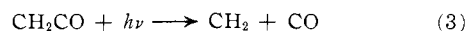hydrogen bond neighboring a carbon–carbon double bond is about one tenth that of addition to the double bond,[6] reaction 1 will be much more preferable than reaction 2. The failure of obtaining cyclopropene may be due partly to the extreme instability of cyclopropene and partly to the enormous energy content of the resulting cyclopropene in reaction 1. If the heats of formation of methylene radical and cyclopropene are taken to be 82[7] and 66.6 kcal./mole,[8] respectively, the heat of reaction of reaction 1 amounts to 71 kcal./mole, indicating the high exothermicity of the reaction. The cyclopropene formed in reaction 1 would have instantly isomerized to methylacetylene and allene in a constant ratio of 1.5. This richness in energy may also be the reason that allene was obtained along with methylacetylene, the latter of which was the only products the thermal isomerization of cyclopropene afforded.[9]

The electronic state of methylene has received considerable attention and it is now almost certain that the methylene produced by the photolysis of diazomethane is at first in a singlet state and then deactivated by collision to a triplet state.[2a,10] Although there are not such explicit data for the methylene produced by the photolysis of ketene, it is likely to be also in a singlet state if the spin conservation rule is applied. In the present study, where no inert gas was present, methylene may have been in its singlet state and reacted with acetylene to produce methylacetylene and allene via excited cyclopropene. That the additions of oxygen and nitric oxide virtually preserved the ratio MA/A unchanged may give support to this view. It is also noteworthy that triplet methylene seems to react with acetylene to give only allene in argon matrix at 4°K.[3c]

Although it is difficult to decide the reaction mechanism at present, a tentative one can be constructed as

$$CH_2CO + h\nu \longrightarrow CH_2 + CO \qquad (3)$$
$$CH_2 + CH_2CO \longrightarrow C_2H_4 + CO \qquad (4)$$
$$\longrightarrow \text{other products} \qquad (4')$$
$$CH_2 + C_2H_2 \longrightarrow C_3H_4'' \qquad (5)$$
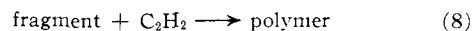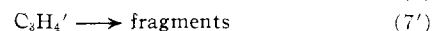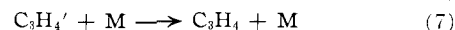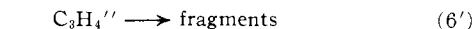$$C_3H_4'' + M \longrightarrow C_3H_4' + M \qquad (6)$$
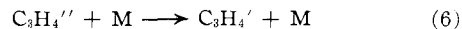
(6) J. N. Butler and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **82**, 759 (1960).

(7) See ref. 12 cited in J. Bell and G. B. Kistiakowsky, *ibid.*, **84**, 3417 (1962).

(8) K. B. Wiberg and W. J. Bartley, *ibid.*, **84**, 3980 (1962).

(9) K. B. Wiberg and W. J. Bartley, *ibid.*, **82**, 6375 (1960).

(10) G. Herzberg, *Proc. Roy. Soc.* (London), **A262**, 291 (1961).

$$C_3H_4'' \longrightarrow \text{fragments} \qquad (6')$$
$$C_3H_4' + M \longrightarrow C_3H_4 + M \qquad (7)$$
$$C_3H_4' \longrightarrow \text{fragments} \qquad (7')$$
$$\text{fragment} + C_2H_2 \longrightarrow \text{polymer} \qquad (8)$$

where C_3H_4 refers to methylacetylene and allene and prime and double prime indicate probably vibrationally excited states. Somewhat similar mechanism containing two deactivation steps has been adopted by Frey and Kistiakowsky[11] in the reaction of methylene with ethylene. Assuming $k_{6MA}/k_6'_{MA} = k_{7MA}/k_7'_{MA} = k_{6A}/k_6'_A = k_{7A}/k_7'_A$, where subscripts MA and A indicate the rate constants for methylacetylene and allene, respectively, the steady-state treatment gives the equations

$$\frac{R_{CO}}{R_{C_2H_4}} = 2 + \frac{k_4'}{k_4} + \frac{k_{5MA} + k_{5A}}{k_4}\frac{[AC]}{[K]} \qquad (III)$$

$$R_{MA}/R_A = k_{5MA}/k_{5A} \qquad (IV)$$

$$\left(\frac{R_{CO}}{R_{MA}}\right)^{1/2} = \left\{\frac{k_{5MA} + k_{5A}}{k_{5MA}} + \frac{k_4}{k_{5MA}}\left(2 + \frac{k_4'}{k_4}\right)\frac{[K]}{[AC]}\right\}^{1/2}\left(1 + \frac{k_6'_{MA}}{k_{6MA}}\frac{1}{[M]}\right) \qquad (V)$$

$$\left(\frac{R_{CO}}{R_A}\right)^{1/2} = \left\{\frac{k_{5MA} + k_{5A}}{k_{5A}} + \frac{k_4}{k_{5A}}\left(2 + \frac{k_4'}{k_4}\right)\frac{[K]}{[AC]}\right\}^{1/2}\left(1 + \frac{k_6'_{MA}}{k_{6MA}}\frac{1}{[M]}\right) \qquad (VI)$$

Equations V and VI well explain the experimentally observed square-root dependences of R_{CO}/R_{MA} and R_{CO}/R_A on the reciprocal of pressure. The value of k_4'/k_4 can be estimated to be 0.2 by applying eq. III to the photolysis of pure ketene in which $[AC] = 0$ and $R_{CO}/R_{C_2H_4}$ is about 2.2 even at the initial stage of the reaction.[5] Comparisons of eq. III and IV with experimental results give the values of 1.1 ± 0.1 and 1.5 ± 0.3 for $(k_{5MA} + k_{5A})/k_4$ and k_{5MA}/k_{5A}, respectively. Although it is also possible to obtain $(k_{5MA} + k_{5A})/k_4$ by comparing eq. V and VI with I and II, the value is very sensitive to the constant term in I and II and the estimation was not made. Nevertheless, it may be said that the reactivity of methylene with acetylene is about the same as that with ketene to give ethylene and carbon monoxide.

(11) H. M. Frey and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **79**, 6373 (1957).

Tritium β-Decay Induced Reactions in the Polystyrene Fluff[1]

By JOHN Y. YANG AND RONALD B. INGALLS

During exposure of polystyrene fluff to tritium gas, tritium becomes incorporated in the polystyrene with an efficiency similar to those reported for vapor phase exposure of light hydrocarbons of analogous structure. The efficiency is increased in the presence of xenon and greatly reduced in the presence of nitric oxide. After exposure, tritium is found predominantly in the aromatic position. The degree of cross linking of the polymer was measured as a function of the β-energy absorbed and was found unaffected by the presence of a number of additive gases. A G(cross link) value of 0.05 was obtained. Free radicals were observed by electron spin resonance simultaneously with the tritium exposure.

Introduction

The Wilzbach gas-exposure method[2] is used widely for tritium labeling of organic compounds otherwise difficult to synthesize. Mechanism studies of such labeling processes have been the subjects of a number of recent investigations.[3–10]

(1) Work performed for the U. S. Atomic Energy Commission under Contract AT(11-1)-GEN-8, and presented in part at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963.

(2) K. E. Wilzbach, *J. Am. Chem. Soc.*, **79**, 1013 (1957).

(3) P. Riesz and K. E. Wilzbach, *J. Phys. Chem.*, **62**, 6 (1958).

(4) A. Y. Mottlau, *ibid.*, **64**, 931 (1960).

(5) K. Yang and P. L. Gant, *J. Chem. Phys.*, **30**, 1108 (1959).

(6) K. Yang and P. L. Gant, *ibid.*, **31**, 1589 (1959).

(7) P. L. Gant and K. Yang, *ibid.*, **32**, 1757 (1960).

(8) T. H. Pratt and R. Wolfgang, *J. Am. Chem. Soc.*, **83**, 10 (1961).

(9) K. Yang and P. L. Gant, *J. Phys. Chem.*, **66**, 1619 (1962).

(10) S. Wexler, *J. Am. Chem. Soc.*, **85**, 272 (1963).

A technique of using polymer fluff, a rigid and finely spaced solid, to facilitate gas–solid reactions has been developed by Ingalls and Wall.[11] In a recent communication,[12] we reported the direct observation of radical intermediates by exposure of polystyrene fluff to tritium gas. The present work has been carried out to establish the structure of the radical intermediates and to elucidate the reaction mechanism in the tritium–polystyrene fluff system.

Experimental

Materials.—Polystyrene was a high purity sample with weight average molecular weight of 1×10^6, furnished by Dr. R. E. Florin of the National Bureau of Standards. Carrier-free tritium gas was obtained from the Oak Ridge National Laboratory and further purified by absorption and desorption in a uranium furnace. Hydrogen gas was purified similarly. Assayed reagent grade helium and xenon were purchased from the Air Reduction Co. and were used without further purification. Matheson nitric oxide was subjected to bulb-to-bulb distillation in a vacuum system and finally withdrawn from a liquid nitrogen cooled bulb by means of a Toepler pump.

Preparation of Polymer Fluff.—Polystyrene was dissolved in reagent grade benzene to the desired concentration. Fluff capsules made from 0.3% solution were cast in thin-walled quartz tubes (5 mm. i.d. × 22 mm. long) by rapid freezing of the solution in a Dry Ice–acetone bath, and followed by removal of the solvent by vacuum sublimation at 0°. Complete removal of benzene from the fluff was achieved by continued evacuation at 50°. Fluff capsules from 1% solution were cast in Pyrex tubes (9 mm. i.d. × 22 mm. long) and removed from the tubes before use.

Tritium Exposure.—Our experimental apparatus consisted simply of a quartz tube connected through a stopcock to a gas reservoir tube. Polystyrene fluff (one 0.3% capsule or four 1% capsules) was placed in the quartz tube, and the reaction vessel was evacuated. Measured amount of tritium gas was withdrawn from a uranium furnace and introduced into the gas reservoir tube through a Toepler pump. Helium, xenon, or hydrogen was added in a similar manner when desired. In cases where nitric oxide was the additive, it was admitted before the introduction of tritium. The reactant gases were mixed by alternate heating and cooling the reservoir loop, before being admitted into the fluff-containing tube by expansion through the stopcock. Upon completion of desired exposure, tritium was re-absorbed in a second uranium furnace. The tritiated fluff was subjected to thorough evacuation before removal for analyses.

Electron Spin Resonance Studies.—The e.s.r. measurements were made at frequencies near 9.5 kMc. using a Varian V4500, X-band e.p.r. spectrometer with 100-kc. modulation. The quartz tube was carefully positioned with the lower fluff capsule centered in the resonance cavity. The background e.s.r. signal was checked before the reaction was allowed to commence. The growth of the e.s.r. signal intensity was then followed as a function of time. Estimation of the radical concentration was made by comparison with a calibrated standard of 0.0001% $Mn(NO_3)_2$ in ZnS (for which we are grateful to Dr. Daniel Kivelson of UCLA).

Radioassay.—Following thorough evacuation, a 1–2-mg. sample of the tritiated fluff was subjected to combustion in an oxygen flask by a modified Schoniger method.[13,14] Resulting water samples were analyzed for tritium activity by means of liquid scintillation counting.

The bulk of each tritiated polystyrene sample was separated into benzene-soluble and benzene-insoluble fractions. Each fraction was subjected to depolymerization by vacuum distillation at 400°. The depolymerized samples were dissolved in styrene and analyzed for tritium activity.

Gas Chromatography–Radioactivity Analysis.—The monomer fraction of the depolymerized fluff sample was isolated by vacuum transfer of the frozen styrene solution, allowing the final temperature to reach 0°. The distillate was examined for radioactive components by means of a Cary–Loenco radioactivity analysis system under varying conditions. The helium elution gas flow rate was maintained at 60 ml./min., and sufficient argon purge gas was used to increase the total gas flow through the 50-ml. ion chamber to 400 ml./min. The major radioactivity distribution was determined by the use of a 2-m. polyester succinate column (0.25 in. o.d.) at 115° and a 2-m. Carbowax 20M column (0.25 in. o.d.) at 130°. The more volatile components were resolved by the use of a 2-m. β,β'-oxydipropionitrile column (0.25 in. o.d.) operating at 50°.

Isotopic Distribution in Styrene.—The carrier styrene was purified by gas chromatography through a 3-m. Carbowax 20M column (3/8 in. o.d.) at 130° with helium flow at 150 ml./min. The purified styrene was converted to benzoic acid by alkaline permanganate oxidation.[15] Benzoic acid was purified by recrystallization from hot water, followed by vacuum sublimation at 115°. The difference in tritium activity between styrene and benzoic acid is attributed to loss of hydrogen atoms from the side chain of the styrene molecule.

Results

The observed e.s.r. spectrum in the tritium–polystyrene fluff system is virtually identical with that observed in γ-irradiated polystyrene[16] and similar to those reported for hydrogen and deuterium atom reactions with the polymer.[17] The e.s.r. signal growth for a series of experiments, using 0.3% polystyrene fluff as the substrate, has been presented graphically in our earlier report.[12] The rates of radical formation obtained in a series of experiments carried out with 1% polystyrene fluff as the reaction matrix are shown in Fig. 1, in which one unit of e.s.r. signal height represents
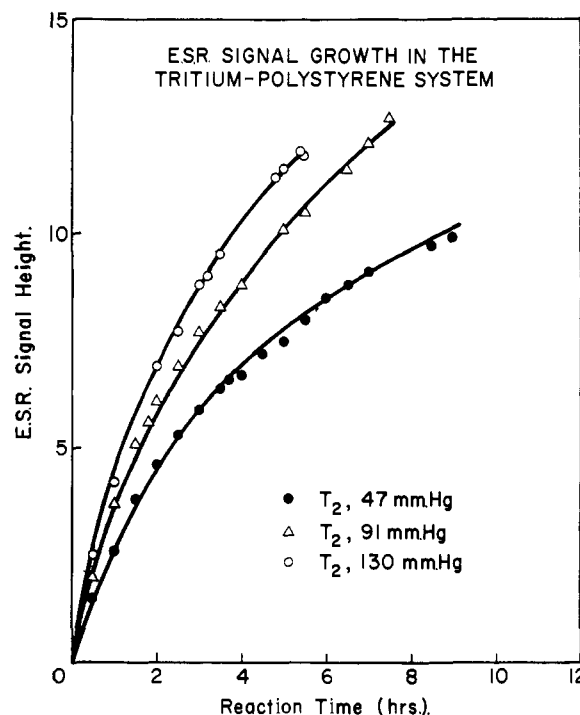

Fig. 1.—Radical formation in the tritium–polystyrene system.

in the order of 10^{14} spins in a sample volume of 1.5 ml. containing about 15 mg. of polystyrene. The initial rate of radical formation is found to be essentially a linear function of tritium concentration, and it is enhanced by the presence of xenon or helium. With nitric oxide as additive, an e.s.r. spectrum developed only after several hundred hours exposure.

Extensive cross linking of the polystyrene resulted by exposure to tritium gas. The data are summarized in Table I. The tritium β-radiation dose was calculated from tritium gas in contact with the fluff by assuming complete absorption of energy in the reaction system. Our assumption is based on the low range of tritium β-particles (7 μ in liquid H_2O) and can be substantiated by estimation from findings of Dorfman[18] on the absorption of tritium β-particles in various gases. It is significant that none of the additives, particularly nitric

(11) R. B. Ingalls and L. A. Wall, *J. Chem. Phys.*, **35**, 370 (1961).

(12) J. Y. Yang, R. B. Ingalls, and J. R. Hardy, *J. Am. Chem. Soc.*, **84**, 2831 (1962).

(13) W. Schoniger, *Mickrochim. Acta*, 123 (1955).

(14) F. Kalberer and J. Rutschmann, *Helv. Chim. Acta*, **44**, 1956 (1961).

(15) L. F. Fieser, "Experiments in Organic Chemistry," 2nd Ed., D. C. Heath and Co., New York, N. Y., 1941, p. 200.

(16) R. E. Florin, L. A. Wall, and W. D. Brown, *Trans. Faraday Soc.*, **56**, 1304 (1960).

(17) R. B. Ingalls and L. A. Wall, *J. Chem. Phys.*, **35**, 370 (1961).

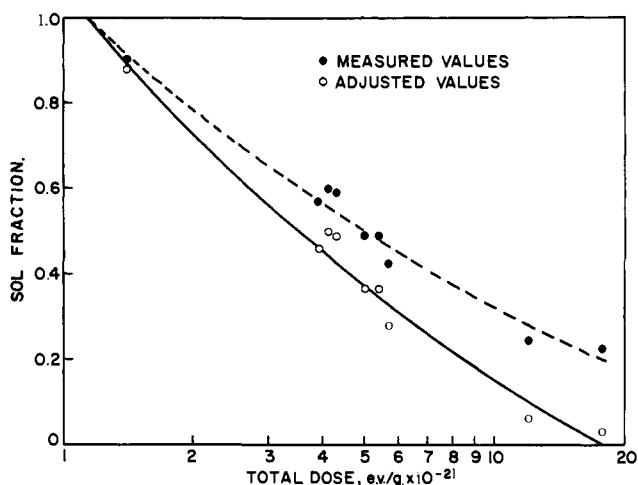(18) L. M. Dorfman, *Phys. Rev.*, **95**, 393 (1954).

Fig. 2.—Dose dependence of polystyrene cross linking.

Fig. 3 (upper) and 4 (lower).—Chromatogram of depolymerized products from tritium exposure of polystyrene.

oxide, showed any effect on the degree of polymer cross linking. Radical combination in a spur created by the tritium β-particle is definitely suggested.

TABLE I

TRITIUM INCORPORATION AND CROSS LINKING IN POLYSTYRENE

T_2, mm.	Additive, mm.	Total dose, e.v./g. $\times 10^{-21}$	G(polymer-T)	Gel, %
130	None	17.7	0.23	77.6
91	None	12.0	.31	75.4
47	None	5.7	.24	57.5
46	None	1.4	.22	9.4
42	Xe, 99	5.4	.69	50.7
44	Xe, 253	5.0	.91	50.8
47	He, 101	4.1	.22	39.5
45	H_2, 132	4.3	.05	40.6
46	NO, 7.0	3.9	.10	43.0

The polymer solubility as a function of the radiation dose is presented in Fig. 2. The failure for the sol fraction value to reach zero at large radiation dose is due not to simultaneous scission,[19] but more likely to a small degree of imperfection[20] in the fluff. By making appropriate allowance, an adjusted solubility vs. dose curve is obtained. From either curve, the gel point is found to be 1.15×10^{21} e.v./g., corresponding to G(crosslink) of 0.05, in agreement with values reported for a variety of different radiations.[19]

The data for tritium labeling of polystyrene are presented in Table I, where the yields are expressed as G(polymer-T), the number of tritium atoms incorporated per 100 e.v. energy. The observed tritium labeling of polystyrene is essentially a first-order function of the tritium pressure. The fraction of activity appearing as benzene-insoluble polymer was determined, and the specific activity in cross-linked polystyrene was found in every case to be about twice that of the noncrosslinked polymer. It is interesting to note the enhanced tritium labeling in the presence of xenon. Nitric oxide inhibited tritium labeling by about 50%. The addition of hydrogen caused a decrease in G(polymer-T) to essentially the same degree as the isotopic dilution factor.

A number of tritium-labeled components were observed in the monomer fraction of depolymerized polystyrene. Figures 3 and 4, in which light lines represent thermal conductivity changes and heavy lines indicate

(19) A. Charlesby, "Atomic Radiation and Polymers," Pergamon Press, New York, N. Y., 1960, pp. 284–289.

(20) Owing to the small range of tritium β-radiation, any aggregation in excess of 10 μ would result in shielding of polymer molecules from the effect of radiation.
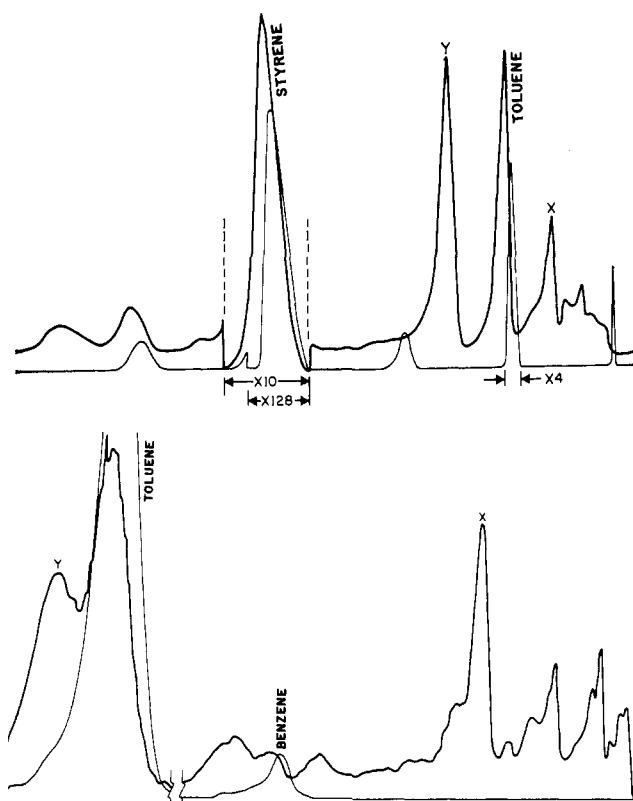
ion-current values, are two gas chromatography-radioactivity recordings of a typical sample. Spectrum A was obtained by the use of a polyester succinate column, and spectrum B obtained with β,β'-oxydipropionitrile as the stationary phase. When nitric oxide was the additive, however, only styrene and toluene activities were detected in significant quantities. Toluene appears as a pyrolytic by-product from depolymerization. The components X and Y as indicated in Fig. 3 and 4 correspond, respectively, to 1,3-cyclohexadiene and vinylcyclohexadiene and are readily eliminated by the presence of nitric oxide in the gaseous reactants.

The data for isotopic tritium distribution in depolymerized styrene monomer are summarized in Table II.

TABLE II

TRITIUM ISOTOPE DISTRIBUTION IN DEPOLYMERIZED STYRENE

T_2, mm.	Additive, mm.	Total dose, e.v. $\times 10^{-20}$	Tritium in aromatic ring, %	
			Sol. fluff	Insol. fluff
47	None	3.3	86	91
46	None	0.8	92	99
42	Xe, 99	3.0	77	72
47	He, 101	2.5	90	92
45	H_2, 132	2.5	91	97
46	NO, 7.0	2.2	95	98

Complete random distribution of tritium in polystyrene would give 62.5% of the activity in the aromatic ring. Our results definitely indicate that the ring hydrogens are preferentially displaced.

Discussion

It is known that for β-decay in gaseous tritium the reaction proceeds with the formation of a recoil ^{3}HeT$^+$ particle. The species ^{3}HeT$^+$ does not dissociate immediately,[21] and it has been shown to contribute

(21) A. H. Snell, F. Pleasonton, and H. E. Lening, J. Inorg. Nucl. Chem., 5, 112 (1957).

significantly to the initiation of isotopic labeling in various tritium and light hydrocarbon systems.[5-8] The average β-energy for tritium decay is 5.67 ke.v. and so the maximum contribution from ^{3}HeT$^+$ initiation would lead to G for tritium incorporation of 0.018. More than 90% of labeling in the tritium–polystyrene fluff system must be accounted by β-radiation processes.

A mechanism for tritium incorporation by radiation-induced intermediates from the tritium molecule has been proposed by Yang and Gant.[6,7] The importance of such processes is apparently magnified in the heterogeneous tritium–polystyrene fluff system. Radiolytic intermediates from polystyrene lead primarily to cross linking of the polymer. The enhancement and reduction in tritium incorporation due, respectively, to the presence of xenon and nitric oxide together with the lack of effect on the polymer cross linking clearly indicate that two independent series of reactions are involved.

Our findings in tritium incorporation are consistent with a mechanism involving both ionic and radical intermediates in a series of well-characterized reactions.

$$T_2 \xrightarrow{\;\beta\;} T_2^+ + e^- \tag{1}$$

$$T_2^+ + T_2 \longrightarrow T_3^+ + T \tag{1a}$$

$$T_2 \xrightarrow{\;\beta\;} T^+ + T + e^- \tag{2}$$
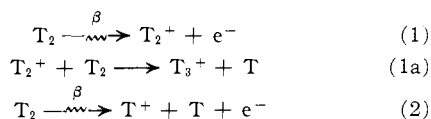
In the presence of an inert gas, the following initiating reaction[22-25] becomes important.

(22) D. P. Stevenson and D. O. Schissler, *J. Chem. Phys.*, **23**, 1353 (1955).

$$X^+ + T_2 \longrightarrow XT^+ + T \tag{3}$$
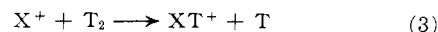
The presence of ionic intermediates is supported by our observed enhancement in tritium incorporation with xenon as additive. The high efficiency for xenon sensitization in reaction 3 has been demonstrated by Lampe.[26] The XeT$^+$ ion is subsequently neutralized,[27] and tritium incorporation proceeds *via* radical intermediates. Both our electron spin resonance observations[28] and the product tritium distribution data indicate that the intermediate radicals are of the cyclohexadienyl type resulting from tritium atom addition to the aromatic ring. Since about 90% of the tritium activity appears as styrene in the depolymerized sample, the preferred termination must take place *via* ring hydrogen atom abstraction by another radical, analogous to the sequence of reactions proposed for hydrogen formation in the radiolysis of toluene.[29]

(23) D. O. Schissler and D. P. Stevenson, *ibid.*, **24**, 926 (1956).
(24) D. P. Stevenson, *J. Phys. Chem.*, **61**, 1453 (1957).
(25) F. W. Lampe, F. H. Fields, and J. L. Franklin, *J. Am. Chem. Soc.*, **79**, 6132 (1957).
(26) F. W. Lampe, *ibid.*, **82**, 1551 (1960).
(27) A. Mascke and F. W. Lampe, *ibid.*, **84**, 4602 (1962).
(28) R. B. Ingalls and D. Kivelson, *J. Chem. Phys.*, **38**, 1907 (1963).
(29) R. B. Ingalls, *J. Phys. Chem.*, **65**, 1605 (1961).

Kinetics of Proton Exchange in Aqueous Solutions of Acetate Buffer

BY Z. LUZ AND S. MEIBOOM

Rates of proton exchange between the carboxyl group of acetic acid and water are reported. The rates were determined from the broadening of the proton magnetic resonance line of water enriched in O^{17}. The observed kinetics are interpreted in terms of proton transfer within a hydrogen-bonded complex consisting of one acetic acid molecule and two water molecules. On the basis of this mechanism a rate constant for the reaction of 4.8×10^7 sec.$^{-1}$ at 25° is calculated.

Introduction

In this paper we report n.m.r. measurements of the rate of proton exchange between the carboxyl group of acetic acid and water. This rate is too high for direct measurement by the n.m.r. technique. In the n.m.r. spectrum of aqueous solutions of acetate buffer the carboxyl protons and the water protons give a single averaged line; careful measurements of the width of this line over a wide range of buffer ratios did not yield a measurable exchange broadening. However, it proved possible to measure the exchange rate by a somewhat indirect way. The method is based on the fact that proton exchange between acetate buffer and water necessarily results in the transfer of protons between water molecules. The contribution of the acetate buffer to the rate of proton exchange in water can be kept in the experimentally accessible range by suitable choice of the buffer concentration and the buffer ratio.

The rate of proton exchange between water molecules can be measured by n.m.r. in water enriched in O^{17}. The latter nucleus has a spin of $^5/_2$ and provides the spin–spin splitting of the proton resonance necessary for exchange broadening of the resonance line. The details of the method have been described previously.[1] The results show that under our experimental conditions (acid/base ratios between 0.1 and 0.01 and

(1) Z. Luz and S. Meiboom, *J. Chem. Phys.*, **39**, 366 (1963).

NaOAc concentrations up to 0.1 M) there is one dominant exchange reaction between the buffer and the water. The rate of this reaction is proportional to the concentration of acetic acid molecules and is much higher than that of the acid dissociation of acetic acid. In analogy with recent findings[2] for benzoic acid–benzoate buffers in methanol, a cyclic proton-transfer mechanism is suggested.

Rate Measurements.—In the present system, proton exchange between water molecules is due to reactions[3] with H$^+$ and OH$^-$

$$H_3O^+ + H_2O \longrightarrow H_2O + H_3O^+ \tag{1}$$

$$OH^- + H_2O \longrightarrow H_2O + OH^- \tag{2}$$
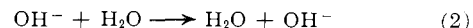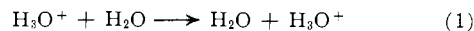
and to reactions between water and either or both of the buffer components, acetic acid and sodium acetate. Since we are interested in the reactions due to the buffer components, we want their contribution to the exchange rate to be dominant or at least comparable to that of reactions 1 and 2. This can be achieved by choosing a buffer ratio such that the pH of the solutions is near 7, where the combined rate of 1 and 2 is a minimum.[3]

The transverse and longitudinal relaxation times of the water protons were measured by the spin echo

(2) E. Grunwald, C. F. Jumper, and S. Meiboom, *J. Am. Chem. Soc.*, **85**, 522 (1963).
(3) S. Meiboom, *J. Chem. Phys.*, **34**, 375 (1961).