filtered, and distilled fractionally through a spinning-band column yielding the pure product, bp 43 °C (lit.[25] bp 43 °C).

***trans*-3-Acetoxy-1-phenylpropene-1** was prepared from cinnamyl alcohol and acetic anhydride,[26] bp 95 °C (5 mm) [lit.[26] bp 135–150 °C (18 mm), 141–142 °C (14 mm)].

3-Acetoxypropene-1 was obtained from allyl alcohol and acetyl chloride in the presence of pyridine,[27] bp 102 °C (lit.[27] bp 103.5 °C).

***trans*-3-Chloro-1-phenylpropene-1** was prepaned from cinnamyl alcohol and hydrogen chloride in CCl_4,[28] bp 104–105 °C (12 mm) [lit.[28] bp 119 °C (17 mm)].

The remaining unsaturated substrates were commercially available and their purity was checked by GLC and NMR.

Kinetics. All kinetic runs were carried out as previously described,[13] following the decrease in 4-chlorobenzenesulfenyl chloride concentration at 385 nm.

Products. 4-Chlorobenzenesulfenyl chloride (20 ml of 0.2 M solution) in acetic acid was added dropwise at 25 °C to 20 ml of 0.2 M solution of an alkene in acetic acid with stirring. The reaction mixture was transferred to a separatory funnel containing 75 ml each of water and benzene. The aqueous layer was removed and the benzene solution was washed with water (100 ml), saturated aqueous $NaHCO_3$ (100 ml), and twice with 100-ml portions of water. After drying ($MgSO_4$), solvent was removed on a rotary evaporator at room temperature. The product composition was then determined in $CDCl_3$.

Elemental Analyses. Attempts to separate the reaction mixtures containing solvent incorporated products by standard methods led to decomposition. Consequently elemental analyses were obtained for only those additions in which no solvent incorporated products were formed. The data are given in Table V.

Registry No.—**1a,** 37973-54-9; **1b,** 21087-29-6; **1c,** 21040-45-9; **1d,** 22688-03-5; **1e,** 4407-36-7; **1f,** 100-42-5; **1g,** 873-66-5; **1h,** 1005-64-7; **2a,** 869-29-4; **2b,** 107-05-1; **2c,** 591-87-7; **2d,** 627-40-7; **2e,** 107-18-6; **2f,** 74-85-1; **2g,** 115-07-1; **2h,** 106-98-9; bromine, 7726-95-6; 4-chlorobenzenesulfenyl chloride, 933-01-7.

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Triphase Catalysis. Applications to Organic Synthesis[1]

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Received September 13, 1976

The triphase catalysis principle, as previously developed for *organic phase–aqueous phase* reactions catalyzed by suitable polystyrene-based catalysts (*solid phase*), has been applied to cyanide ion displacement on activated (benzylic) as well as unactivated organic halides and provides a convenient and effective method of preparation of the corresponding nitriles. Other useful transformations to which the triphase catalysis technique has been successfully applied are the synthesis of ethers, dichlorocyclopropanes, organic chlorides, bromides, and iodides as well as the dehalogenation of *vic*-dibromides and oxidation of alcohols.

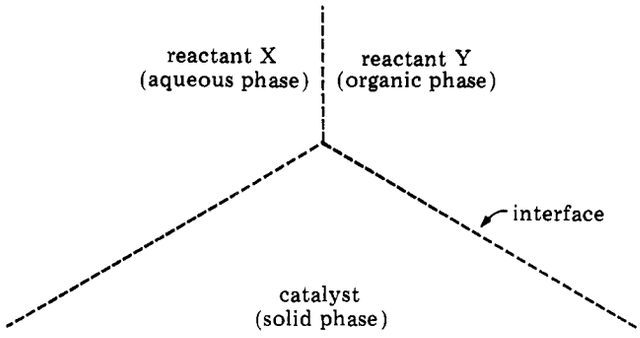
A significant and recurring problem in organic synthesis stems from the use, or desired use, of a water-soluble reagent in chemically altering a water-insoluble organic substrate. If the reaction is conducted as a heterogeneous process (e.g., organic phase–aqueous phase reaction) observed reaction rates are normally very slow owing to the low concentration of at least one of the reactants in each phase. Techniques currently available to circumvent this problem rely on the use of rapid stirring, cosolvent, and phase-transfer methods. If chemical reaction takes place at a liquid–liquid phase boundary, rapid stirring may have an accelerating effect by increasing interfacial contact.[2] Alternatively, the addition of a cosolvent can bring about a homogeneous state and thereby completely eliminate phase separation. Although this latter approach is often useful, product mixtures are necessarily made more complex and the resulting workup made more difficult. In addition, with aqueous phase–organic phase reactions, use of a cosolvent not only renders the organic substrate accessible to the reagent, but also increases the substrate's contact with water and can promote competing hydrolytic pathways. Recently, a third technique has been developed which appears to have considerable potential; this method has been referred to as phase-transfer catalysis.[3] In brief, an organic-soluble, partially water-soluble catalyst (most commonly a tetraalkylammonium or tetraalkylphosphonium salt) accelerates an aqueous phase–organic phase reaction, presumably, by extracting a given ionic reagent out of water and into the bulk organic phase where reaction can ensue.[4] Based on enhanced reaction rates, high yields of products, and the convenience found with this method, it seems likely that many industrial applications will be forthcoming. One practical limitation to the phase-transfer method, however, is that many of the catalysts used promote the formation of stable emulsions.

It occurred to us that the development of a technique centering around the use of a solid phase catalyst to accelerate

aqueous–organic phase reactions (triphase catalysis) would have considerable advantages over those methods described above (Scheme I). Not only would catalyst recovery and

Scheme I

triphase catalysis



product isolation be greatly simplified, but also, owing to the three-phase nature of the system, continuous flow methods could be employed making the technique particularly attractive for industrial applications.

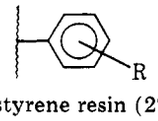
We have previously demonstrated the feasibility of triphase catalysis for the displacement of cyanide ion (aqueous phase) on 1-bromooctane (organic phase) catalyzed by suitable polystyrene ion exchange resins (solid phase).[5,6] The work described in this paper was carried out in order to expand the scope of this technique by applying it to a variety of useful synthetic transformations.

Results and Discussion

Synthesis of Nitriles. Nucleophilic displacement by cyanide ion on organic halides represents the most commonly used method for the preparation of nitriles. Despite the usefulness of this approach, however, the required use of water and/or other polar and potentially nucleophilic solvents needed to dissolve both the cyanide salt and the organic substrate introduces distinct limitations. In particular, competing hydrolysis and ether formation can lead to low yields of nitrile.[7] Phase-transfer catalysis procedures have been successfully utilized in cyanide displacement reactions involving simple alkyl halides.[4,9] Durst has recently reported that phase-transfer catalyzed cyanide displacement on activated halides, e.g., benzyl chloride (or bromide), gave significantly higher yields of nitrile when conducted as liquid–solid rather than liquid–liquid systems.[10]

We have found that triphase catalysis, as previously developed for the displacement of cyanide ion on 1-bromooctane (eq 1),[5] provides a simple and effective means for converting

$$\underset{\text{(organic phase)}}{n\text{-}C_8H_{17}Br} + \underset{\text{(aqueous phase)}}{NaCN} \xrightarrow[\text{(solid phase)}]{\mathbf{1a}} \underset{\text{(organic phase)}}{n\text{-}C_8H_{17}CN} + \underset{\text{(aqueous phase)}}{NaBr} \quad (1)$$



cross-linked polystyrene resin (2% divinylbenzene)

1a, R = $CH_2N(CH_3)_2(n\text{-}C_4H_9)Cl$; 12% ring substitution
b, R = $CH_2N(CH_3)_3Cl$; 12% ring substitution
c, R = $CH_2N(CH_3)_3Cl$; 76% ring substitution
d, R = $CH_2N(CH_3)_3Cl$; 70% ring substitution

activated (benzylic) as well as unactivated organic halides to their corresponding nitriles (Table I).

In addition to the synthetic significance of these results, the observation that competing hydrolytic pathways are not important suggests that the microenvironment of the reactive sites along the polymer backbone is predominantly nonaqueous.[11]

Halogen Exchange. Although many procedures are available for exchanging halogen in organic halides, few have proven useful for converting alkyl bromides to alkyl chlorides.[12,13] We have found that the triphase catalysis technique furnishes a very convenient method for carrying out such transformations. Examples illustrating the utility of triphase catalyzed halogen exchange are provided in Table I. The fact that no significant yield of hydrolysis products could be detected with benzyl bromide and benzyl chloride as the substrates, and also the observation that catalyst activity of the resin falls off with increasing percent ring substitution (compare resins **1a–d**),[14] suggest here, too, that the microenvironment of the reactive sites in the polymer matrix is largely nonaqueous.

Synthesis of Ethers. Conventional methods for the preparation of alkyl and aryl ethers are many in number.[15] Despite this fact, considerable effort is still being expended in developing new and more convenient procedures.[16–19] In order to determine the applicability of triphase catalysis to the synthesis of ethers, we have examined the displacement by phenoxide ion and *n*-butoxide ion, generated by treatment with aqueous sodium hydroxide, on 1-bromobutane dissolved in toluene catalyzed by **1a**. In each case, useful triphase catalytic systems were achieved. As in the cases of cyanide displacement and halogen exchange, resin activity is reduced significantly upon increasing the concentration of quaternary ammonium groups along the polymer backbone.

Synthesis of Dichlorocyclopropanes. Dichlorocarbene addition to alkenes provides an attractive route to dichlorocyclopropanes.[20–22] We have found that dichlorocarbene can be conveniently generated by the addition of **1a** to mixtures of 50% aqueous sodium hydroxide and chloroform at 25 °C. When an appropriate alkene is added to the mixture, high yields of the corresponding dichlorocyclopropane are formed. Tabushi has reported the use of dichlorocarbenes in the conversion of certain alcohols to alkyl chlorides.[23] We have also found that dichlorocarbene generated under triphase conditions is also capable of carrying out similar transformations (Table I).

Dehalogenation of *vic*-Dibromides. Dehalogenation of *vic*-dibromides to alkenes can be carried out through the use of a variety of reagents.[24–26] More recent procedures have relied on the use of sodium thiosulfate[27] and combinations of sodium iodide and sodium thiosulfate.[28] Dehalogenation of certain *vic*-dibromides can also be carried out under triphase conditions employing catalytic amounts of sodium iodide, **1a**, and an excess of sodium thiosulfate at 110 °C as described in the Experimental Section. Stereochemical studies conducted with *meso*- and *dl*-stilbene dibromide[29] indicated a completely stereospecific trans debromination with the former leading to exclusively *trans*-stilbene and a predominantly trans debromination for the *dl* isomer yielding *cis*-stilbene as the major alkene component. Control experiments outlined in the Experimental Section indicate a moderate instability of *cis*-stilbene with regard to isomerization under debromination conditions, suggesting even a higher degree of stereospecificity in the dehalogenation of *dl*-stilbene dibromide.

Oxidation of Alcohols. Attempted reaction of a toluene solution of cyclododecanol with 10% aqueous sodium hypochlorite in the presence of **1d** yielded no observable cyclododecanone even after heating for 70 h at 50 °C.[30] When resin **1a** was suspended at the interface of similar heterogeneous mixtures, however, a triphase catalytic oxidation system was established.

Table I. Synthetic Applications of Triphase Catalysis

Transformation	Reactant	Registry no.	Product	Registry no.	Catalyst	Temp, °C	Time, h	Yield,[a] %
Cyanide displacement	Benzyl chloride	100-44-7	Benzyl cyanide	140-29-4	**1a**	110	15	95
	Benzyl bromide	100-39-0						85
	4-Chlorobenzyl chloride	104-83-6	4-Chlorobenzyl cyanide	140-53-4				88
	4-Bromobenzyl bromide	589-15-1	4-Bromobenzyl cyanide	16532-79-9				99
	4-Methylbenzyl chloride	104-82-5	4-Methylbenzyl cyanide	2947-61-7				92
	1-Bromooctane	111-83-1	1-Cyanooctane	2243-27-8				98
					1b			95
					1c			0
					1d			0
	1-Chlorooctane	111-85-3			**1a**			50
Halogen exchange	1-Bromooctane		1-Chlorooctane				70	97
	1-Chlorooctane		1-Bromooctane				280	54
	Benzyl chloride		Benzyl bromide				24	72
	Benzyl bromide		Benzyl chloride					97
	1,4-Dibromobutane	110-52-1	1,4-Dichlorobutane	110-56-5			60	97
	1-Bromobutane	109-65-9	1-Chlorobutane					87
	1-Bromobutane		1-Iodobutane					90
	1-Chlorobutane	109-69-3	1-Bromobutane					32
	1-Chlorobutane		1-Iodobutane					72
	1-Iodobutane	542-69-8	1-Chlorobutane					59
	1-Iodobutane		1-Bromobutane				70	50
	1-Bromodecane	112-29-8	1-Chlorodecane	1002-69-3			100	94
							240	93[b]
					1b		24	40
					1c			0
					1d			0
Dichlorocarbene addition	α-Methylstyrene	300-57-2	1,1-Dichloro-2-methyl-2-phenylcyclopropane	3591-42-2	**1a**	25	72	99
	trans-β-Methylstyrene	873-66-5	1,1-Dichloro-*trans*-2-methyl-3-phenylcyclopropane	60434-40-4			48	100
	Styrene	100-42-5	1,1-Dichloro-2-phenylcyclopropane	2415-80-7			48	99
	Cyclohexene	110-83-8	7,7-Dichlorobicyclo[4.1.0]heptane	823-69-8			96	98
					1d			15
Dichlorocarbene chlorination	Benzyl alcohol	100-51-6	Benzyl chloride		**1a**		48	67
	1-Adamantyl alcohol	768-95-6	1-Adamantyl chloride	935-56-8			120	25
Alkoxide and phenoxide displacement[c]	1-Butanol	71-36-3	*n*-Butyl ether	142-96-1			24	19
	Phenol	108-95-2	*n*-Butyl phenyl ether	1126-79-0		90	10	97
Dehalogenation of *vic*-dibromides	1,2-Dibromooctane	6269-92-7	1-Octene	111-66-0	**1a**	110	48	15
								1[d]
								0.2[e]
					1a		60	20
	dl-Stilbene dibromide	13027-48-0	*trans*-Stilbene	103-30-0			40	35
			cis-Stilbene					49
			trans-Stilbene		**1d**		40	2
			cis-Stilbene					1
	meso-Stilbene dibromide[f]	13440-24-9	*trans*-Stilbene		**1a**		12	100
			cis-Stilbene					0
	cis-Stilbene[g]	645-49-8	*trans*-Stilbene				40	11
			cis-Stilbene					89
Oxidation of alcohols	Benzyl alcohol		Benzaldehyde	100-52-7		50	50	51
	1-Octanol	111-87-5	Octanal	124-13-0			70	5
	Cyclododecanol	1724-39-6	Cyclododecanone	830-13-7				34
					1d			0

[a] Yields are determined by GLC based upon the reactant. [b] Isolated yield. [c] Alkoxide and phenoxide displacement reactions employ *n*-bromobutane as the alkylating agent. [d] Reaction carried out in the absence of sodium iodide. [e] Reaction carried out in the absence of **1a**. [f] Solvent used as organic phase was 1,1,2,2-tetrachloroethane. [g] Attempted isomerization of *cis*-stilbene (100% initial isomer purity) under debromination conditions.

Experimental Section

General Methods. Unless stated otherwise, all reagents were obtained commercially and were used without further purification. Chloromethylated polystyrene beads (2% divinylbenzene, 200–400 mesh) were obtained from Bio-Rad Laboratories and were used without further purification. *N,N*-Dimethyl-*n*-butylamine was available from K & K Laboratories and used as obtained. All alkyl and benzyl halides and their corresponding nitriles as well as styrene, α-methylstyrene, *trans*-β-methylstyrene, cyclohexene, benzyl alcohol, 1-adamantyl alcohol, *n*-butyl ether, *n*-butyl phenyl ether, *trans*-stilbene, 1-octene, and phenol were purchased from Aldrich Chemical Co. and used as obtained. We are grateful to our colleague Michael McKinney for gifts of 1,1-dichloro-2-methyl-2-phenylcyclopropane and 1,1-dichloro-*trans*-2-methyl-3-phenylcyclopropane. 1,1-Dichloro-2-phenylcyclopropane[22] and 7,7-dichlorobicyclo[4.1.0]heptane[31] were prepared using established procedures. 1,2-Dibromooctane,[32] *cis*-stilbene,[33] *meso*-stilbene dibromide,[34] and *dl*-stilbene dibromide[34] were also prepared using methods previously described in the literature. Benzene, toluene, and tetrahydrofuran were each purified by distillation from sodium and benzophenone under a nitrogen atmosphere. All ^{1}H NMR spectra were recorded using a Varian A-60 spectrometer. Product mixtures were analyzed by GLC on a Hewlett-Packard Model 5710A flame ionization instrument using either a 1.7 ft × 0.125 in. UCW-98 on Chromosorb W column or a 4 ft × 0.125 in Carbowax on Chromosorb P column. The GLC instrument was also equipped with a Hewlett-Packard Model 3380A integrator. Appropriate response factors relative to an internal standard were determined for each different substance analyzed. The temperature of the oil bath was controlled with the aid of a "Therm-O-Watch" Electronic Controller Model L6-1000 (I^2R Co., Cheltenham, Pa.) attached to a thermometer. Culture tubes (Corning no. 9826, 13 × 100 mm) equipped with Teflon-lined screw caps were used as reaction vessels. Microanalyses were performed by Midwest Microlab, Inc., Indianapolis, Ind.

Resin Catalysts 1a–d. Resins catalysts **1a, 1b,** and **1c** were prepared employing procedures previously described.[6] Resin **1d** was commercially available from Bio-Rad Laboratories.

Displacement of Cyanide Ion on Organic Halides. Procedures similar to that described for the conversion of 4-bromobenzyl bromide to 4-bromobenzyl cyanide were followed for all of the nitrile forming reactions described in Table I. To a Corning no. 9826 culture tube containing 0.09 g of **1a** was added a solution of 0.8 g (16.3 mmol) of sodium cyanide dissolved in 2.5 ml of distilled water followed by 0.063 g (0.250 mmol) of 4-bromobenzyl bromide plus 2 ml of toluene. An internal standard (*n*-dodecane) was added to the reaction mixture and the tube was shaken vigorously for 2 min, placed in an oil bath maintained at 110 °C for 15 h, withdrawn, and cooled to room temperature. Analysis of the organic phase by GLC using a UCW-98 on Chromosorb W column indicated a 99% yield of 4-bromobenzyl cyanide.

Halogen Exchange. Procedures similar to that described for the conversion of 1-bromodecane to 1-chlorodecane were followed for all of the small-scale halogen exchange reactions described in Table I. To a Corning no. 9826 culture tube containing 0.08 g of **1a** was added a solution of 0.67 g (11.6 mmol) of sodium chloride dissolved in 2 ml of distilled water followed by 0.069 g (0.31 mmol) of bromodecane plus 2 ml of toluene. An internal standard (*n*-dodecane) was added to the reaction mixture and the tube was sealed with a Teflon-lined screw cap, shaken vigorously for 2 min, placed in an oil bath maintained at 110 °C for 100 h, withdrawn, and cooled to room temperature. Analysis of the organic phase by GLC (Carbowax column) indicated a 94% yield of 1-chlorodecane.

For conversion to organic bromides and iodides, aqueous solutions of sodium bromide and sodium iodide, respectively, were used.

Preparative Scale Conversion of 1-Bromodecane to 1-Chlorodecane. A mixture of 2.3 g (10.4 mmol) of 1-bromodecane dissolved in 20 ml of benzene, 27.0 g (465.5 mmol) of sodium chloride dissolved in 80 ml of water and 0.5 g of **1a** was sealed in a 125-ml Pyrex tube and was placed in an oil bath, maintained at 110 °C for 240 h, withdrawn, cooled to room temperature, and filtered. The resin was washed with 100 ml of benzene and the combined organic phase dried (Na_2SO_4) and concentrated by rotary evaporation leaving a liquid (1.8 g) which was found to be 1-chlorodecane having a ^{1}H NMR spectrum and GLC retention time indistinguishable from those of an authentic sample. Further GLC analysis revealed that the product contained 5% 1-bromodecane.

Dichlorocarbene Addition to Alkenes. Procedures similar to that described for the conversion of α-methylstyrene to 1,1-dichloro-2-methyl-2-phenylcyclopropane were followed for all of the dichlorocyclopropane syntheses described in Table I. α-Methylstyrene (0.118 g, 1.0 mmol) dissolved in 2 ml of chloroform (spectrophotometric grade) was added to 2 ml of 50% aqueous sodium hydroxide solution, plus **1a** (0.1 g) contained in a no. 9826 culture tube. After addition of an internal standard (*n*-dodecane) the mixture was shaken vigorously for 5 min and allowed to remain at 25 °C for 72 h. Analysis of the organic phase by GLC (UCW-98 column) indicated a 99% yield of 1,1-dichloro-2-methyl-2-phenylcyclopropane. Procedures used for conversion of alcohols to alkyl chlorides were similar to that described above except that α-methylstyrene was replaced by the appropriate alcohol.

Phenoxide Displacement on 1-Bromobutane. To a Corning no. 9826 culture tube containing 0.1 g of **1a** was added 2 ml of 2.5 M sodium hydroxide followed by 0.094 g (1.0 mmol) of phenol in 2 ml of toluene, 0.206 g (1.5 mmol) of 1-bromobutane, and an internal standard (*n*-decane). The mixture was shaken vigorously for 5 min and placed in an oil bath maintained at 90 °C for 10 h, withdrawn, and cooled to room temperature. Analysis of the organic phase by GLC (UCW-98 column) indicated a yield of *n*-butyl phenyl ether of 97% based on starting phenol.

***n*-Butoxide Displacement on 1-Bromobutane.** 1-Butanol (0.074 g, 1.0 mmol) dissolved in 2 ml of toluene was added to 2 ml of 50% aqueous sodium hydroxide solution plus **1a** (0.1 g) contained a no. 9826 culture tube. After addition of an internal standard (*n*-dodecane) the mixture was shaken vigorously for 5 min and allowed to remain at 25 °C for 24 h. Analysis of the organic phase by GLC (Carbowax column) indicated a yield of *n*-butyl ether of 20%.

Dehalogenation of *vic*-Dibromoalkanes. Procedures similar to that described for the conversion of *dl*-stilbene dibromide to a mixture of *cis*- and *trans*-stilbene were followed for all debromination experiments. A heterogeneous mixture of *dl*-stilbene dibromide (0.088 g, 0.259 mmol) dissolved in 2 ml of toluene, sodium iodide (0.005 g, 0.033 mmol), and sodium thiosulfate ($Na_2S_2O_3{\cdot}5H_2O$; 1.0 g, 4.0 mmol) dissolved in 2 ml of water and 0.15 g of **1a** along with an internal standard (*n*-dodecane) was sealed in a culture tube shaken vigorously for 5 min and placed in an oil bath, maintained at 110 °C. After a reaction time of 40 h, the tube was withdrawn and cooled to room temperature. Analysis of the organic phase by GLC (UCW-98) indicated a 35% yield of *trans*-stilbene plus a 49% yield of *cis*-stilbene.

Oxidation of Cyclododecanol. Cyclododecanol (0.055 g, 0.3 mmol) dissolved in 2 ml of toluene was added to 5 ml of 10% aqueous sodium hypochlorite (commercial swimming pool bleach) plus **1a** (0.05 g) contained in culture tube. After addition of an internal standard (*n*-octadecane), the mixture was shaken vigorously for 5 min and heated to 50 °C for 70 h. Analysis of the organic phase by GLC (Carbowax column) indicated a 34% yield of cyclododecanone.

Procedures similar to that described above were used for all oxidation reactions described in Table I.

Acknowledgment. We are grateful to Ms. Linda Dulak for providing some technical assistance throughout the course of this investigation.

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One-Electron Redox Reactions of Water-Soluble Vitamins. 4. Thiamin (Vitamin B_1), Biotin, and Pantothenic Acid

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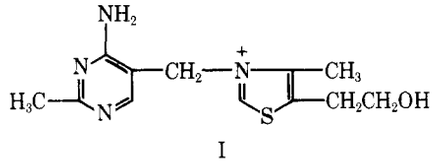
Received February 27, 1976

The technique of pulse radiolysis and kinetic absorption spectrophotometry was used to study the one-electron reduction of thiamin, thiazole, 4-aminopyrimidine, biotin, and pantothenic acid in aqueous solution. The acetone ketyl radical and e_{aq}^- were used as the one-electron reducing agents. The reaction rate constants of e_{aq}^- and $(CH_3)_2\dot{C}OH$ with these compounds were determined at different pH values, taking into account the dissociation constants of the substrates. The transient optical absorption spectra of the intermediates produced, their extinction coefficients, decay kinetics, and ionization constants were determined. For thiazole (Tz), the radical formed in neutral solution (·TzH) has a λ_{max} 317 nm, ϵ_{317} 3.8×10^3 M^{-1} cm^{-1}, decays with $2k \sim 2 \times 10^8$ M^{-1} s^{-1}, and has a pK_a (radical) = 3.1. This is close to that of the parent compound, pK = 2.5. For 4-aminopyrimidine (4-Am-Pm), the radicals formed have maxima at λ <260 nm, and the pK_a of the dihydro radical cation 4-Am-PmH_2·$^+$ is 6.4. Thiamin in neutral solution forms intermediates with maxima at 317 and 350 nm, and $\epsilon \sim 6.5 \times 10^3$ M^{-1} cm^{-1}. One-electron reduction of the thiazolium ring of thiamin is suggested, based on the formation of dihydrothiamin as a final product. Other assignments for these radicals are suggested and discussed. The reaction of OH radicals with biotin and pantothenic acid leads, primarily, to H atom abstraction at various sites in the molecule. The formation and ionization of the $-\dot{C}(OH)CONH-$ radical from pantothenic acid, pK_a = 6.0 ± 0.3, is proposed.

Thiamin (vitamin B_1, I), in the form of its pyrophosphate (at OH group), is the coenzyme for a number of biochemical reactions involved in carbohydrate metabolism, e.g., cleavage



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of carbon–carbon bonds adjacent to carbonyl compounds (as in pyruvic acid).[2,3] Many common foods contain appreciable quantities of thiamin. Thiamin contains a pyrimidine and a thiazole nucleus. The activity of this vitamin is probably linked primarily to the thiazolium ring.[4] Reduction (hydrogenation) of the thiazolium ring results in a complete loss of activity. The mechanism of thiamin action has been suggested[4] to involve the ionization of the thiazolium ring, through the loss of a proton from the C_2 carbon, resulting in the formation of a zwitterion. Biotin (vitamin H) serves as an acceptor molecule for bicarbonate ion in enzymes which catalyze several biosynthetic reactions.[5] The function of the sulfur atom in biotin is still not well characterized. Protonation of biotin, $pK_2 = -1.1$ ($pK_a \sim 4.8$ for the –COOH), has been suggested[6] to occur on the ureido group, presumably on the carbonyl oxygen atom. More recent results indicate that there is no sulfur–carbonyl transannular interaction in biotin (see ref 6, 7). Pantothenic acid[2] is a component of coenzyme A, functions in acetylation reactions in amino acid, carbohydrate, and fat metabolism, and is involved in various biosynthesis with other vitamins.

The fast-reaction technique of pulse radiolysis and kinetic absorption spectrophotometry was used to study the one-electron reduction of these vitamins and related compounds in water. The hydrated electron and the acetone ketyl radical were used as one-electron reducing agents. The reactions with OH radicals were also examined. The results obtained are reported below.

Experimental Section

The pulse radiolysis setup[8,9] and the experimental conditions used have been described.[10] The one-electron reduction of the compounds was brought about by reaction with e_{aq}^- and/or $(CH_3)_2\dot{C}OH$ radicals. The necessary conditions for these experiments have already been described.[10,11]

The extinction coefficients given below are based on $G(e_{aq}^-) = G(OH) = 2.8$. Dosimetry[8] was carried out using KCNS. The transient spectra presented were corrected for depletion of the ground-state absorption of the molecules.

The chemicals used were the highest purity commercially available and were obtained from Calbiochem, Cyclochemicals, and Sigma Chemicals. The reagents used were purchased from Mallinckrodt, Baker and Adamson, Aldrich, and Eastman Chemicals. Solutions were buffered using perchloric acid, potassium hydroxide, phosphate, and tetraborate.

Results and Discussion

Reactivity toward e_{aq}^-, $(CH_3)_2\dot{C}OH$, and OH Radicals. The reaction rate constants of e_{aq}^- with thiazole, 4-aminopyrimidine, and thiamin were determined at pH 6–8, taking