nitrile) (10 mg) was irradiated as described above. The mixture was cooled in ice and treated with bromine until the latter was in slight excess, which was then removed by washing with aqueous sodium metabisulfite. After being diluted with pentane (5 mL) the mixture was chromatographed on silica gel. Elution with pentane removed the tin compounds, and the deuterated ester (0.45 g, 90%) was obtained essentially pure upon elution with ether/pentane (1:4): ^{1}H NMR δ (CCl_4) 3.63 (s, 3 H), 2.42–2.12 (m, 2 H), 2.12–1.67 (m, 6 H), 1.67–1.43 (m, 2 H). Hydrolysis of the ester to 5-deuteriobicyclo[3.1.1]heptane-1-carboxylic acid (0.35 g, 85%) was effected by methanolic potassium hydroxide at 50 °C for 2 h. The acid had spectral data in accord with those observed for the protio isomer.[20]

1-Deuteriobicyclo[3.1.1]heptane (3a). 5-Deuteriobicyclo[3.1.1]heptane-1-carboxylic acid (0.34 g, 2.5 mmol) and freshly distilled thionyl chloride (2.5 mL) were heated under reflux for 2 h. Excess reagent was removed in vacuo and the crude acid chloride was dissolved in a mixture of dichloromethane (1 mL) and anhydrous pyridine (0.5 mL) and cooled in an ice bath. *tert*-Butyl hydroperoxide (1.5 mL, 4.3 mmol) in 1,2-dichloroethane was added dropwise to the stirred mixture maintained at 0 °C. After 3 h the contents were poured on to ice–water and extracted with dichloromethane. The combined organic fractions were washed with cold, dilute sulfuric acid, water, and finally cold aqueous sodium carbonate, before being dried ($MgSO_4$). Filtration through Florisil followed by evaporation of solvent yielded *tert*-butyl 5-deuteriobicyclo[3.1.1]heptane-1-peroxycarboxylate (0.42 g, 79%); ^{1}H NMR δ (CCl_4) 2.50–2.13 (m, 2 H), 2.13–1.88 (m, 6 H), 1.88–1.47 (m, 2 H), 1.27 (s, 9 H). The peroxy ester was added to triisopropylbenzene (2 mL) and the mixture heated at 110 °C for 2 h. Volatile products were swept into a cold trap by a gentle stream of nitrogen, and the byproducts contaminating the hydrocarbon were removed by washing with water. 1-Deuteriobicyclo-[3.1.1]heptane (0.11 g, 58%) had physical properties consistent with those of the unlabeled hydrocarbon.[17]

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Registry No. 1a (unlabeled), 280-33-1; **1b** (unlabeled), 19074-26-1; **1c** (unlabeled), 699-55-8; **2a** (unlabeled), 279-23-2; **2b** (unlabeled), 10052-18-3; **2c** (unlabeled), 18720-30-4; **3a** (unlabeled), 286-34-0; **3a** (labeled), 91239-73-5; **3b** (unlabeled), 87969-60-6; **3c** (unlabeled), 91239-72-4; **4a** (unlabeled), 285-86-9; **4a** (labeled), 91239-74-6; **4b** (unlabeled), 17065-20-2; **4c** (unlabeled), 64725-77-5; **5a** (unlabeled), 311-75-1; **5b** (unlabeled), 10555-48-3; **5c** (unlabeled), 22287-28-1; 5-deuteriobicyclo[3.1.1]heptane-1-carboxylic acid, 91239-75-7; 1-bromobicyclo[2.1.1]hexane, 77379-00-1; methyl 5-bromobicyclo[3.1.1]heptane-1-carboxylate, 91239-76-8; methyl 5-deuteriobicyclo[3.1.1]heptane-1-carboxylate, 91239-77-9; 5-deuteriobicyclo[3.1.1]heptane-1-carbonyl chloride, 91239-78-0; *tert*-butyl hydroperoxide, 75-91-2; *tert*-butyl 5-deuteriobicyclo[3.1.1]heptane-1-peroxycarboxylate, 91265-45-1.

Carbon Kinetic Isotope Effects on the Hydration of Carbon Dioxide and the Dehydration of Bicarbonate Ion

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Abstract: ^{13}C kinetic isotope effects on the hydration of CO_2 and the dehydration of HCO_3^- in aqueous solution have been measured by rapid removal of the product and conversion to an isotopically stable form, followed by isotope-ratio analysis. The isotope effect on hydration is $k^{12}/k^{13} = 1.0069 \pm 0.0003$ at 24 °C. The isotope effect on dehydration is 1.0147 ± 0.0007. The ratio of these two values gives an equilibrium isotope effect of $K^{12}/K^{13} = 1.0077$, in good agreement with previously measured values. The small magnitudes of the kinetic isotope effects indicate that the transition state for conversion of HCO_3^- to CO_2 is very similar to that of HCO_3^-. This information together with previously measured solvent isotope effects indicates that the mechanism of HCO_3^- dehydration probably involves general-acid-catalyzed donation of a proton from H_3O^+ to the departing oxygen, rather than unimolecular decomposition of the zwitterion H_2O^+–CO_2^- in the rate-determining step.

The isotopic chemistry of processes involving carbon dioxide is important in connection with studies in chemistry, biochemistry, geochemistry, and plant physiology. Equilibrium isotope fractionations have been measured for the liquefication of CO_2,[1] the dissolution of gaseous CO_2 in water,[2,3] the conversion of CO_2 into HCO_3^- (ref 4), and the incorporation of CO_2 into the carboxyl groups of organic compounds.[5] Kinetic isotope fractionations have been reported for chemical decarboxylations,[6] enzymatic decarboxylations,[7] enzymatic carboxylations,[8] and diffusion processes.[3] However, isotope effects have not yet been measured for one of the very simplest and potentially most important reactions involving CO_2, namely, the hydration of CO_2 and its reverse, the dehydration of HCO_3^-.

Carbon isotope fractionation accompanying the hydration of CO_2 is potentially of importance in plants, particularly in C4 plants and in CAM plants during nocturnal CO_2 fixation, wherein atmospheric CO_2 must be converted to HCO_3^- prior to fixation by phosphoenolpyruvate (PEP) carboxylase.[9] Although it is generally assumed that carbonic anhydrase levels in plants are high and that

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Scheme I

$$CO_2(g) \rightleftharpoons CO_2(aq) \rightarrow HCO_3^- \xrightarrow{\text{PEP, PEP carboxylase}} \text{oxalacetate} \xrightarrow{\text{NADH, malate dehydrogenase}} \text{malate}$$

the kinetics of CO_2 hydration are not significant for limiting photosynthesis,[10] recent isotopic evidence indicates that this may not always be so.[11]

The nonenzymatic hydration of CO_2 near neutral pH occurs by direct reaction of CO_2 with H_2O. Above pH 8, reaction of CO_2 with OH^- may also occur.[12,13] General-base catalysis of the reaction of CO_2 with H_2O can also be observed under certain circumstances.[13,14]

In this paper we report the development of methodology which enables us to measure carbon isotope effects on the hydration of CO_2 and the dehydration of HCO_3^-. Study of both reactions is particularly useful because the ratio of the two isotope effects should equal the known equilibrium isotope effect, thus providing a check on the adequacy of our experimental procedures.

Experimental Section

Malate dehydrogenase, malic enzyme, glutathione reductase, phosphoenolpyruvate (PEP), NADH, NADP, malic acid, and *N*-(2-hydroxyethyl)piperazine-*N'*-2-ethanesulfonic acid (HEPES) were obtained from Sigma Chemical Co. PEP carboxylase was prepared as previously described.[8a] The enzyme preparation had a specific activity of 10–15 μmol/mg of protein/min. N_2 and He were purified by passing laboratory grade materials through a column of Ascarite. D_2O was obtained from Stohler Chemical Co. $^{13}CO_2$ (95% ^{13}C) and $H_2{}^{18}O$ (97% ^{18}O) were obtained from Mound Laboratories, Miamisburg, OH. $^{13}C^{18}O_2$ was synthesized by exchange as previously described.[11]

^{13}C NMR spectra were measured on a JEOL FX-200 NMR spectrometer. Spectrophotometric assays were conducted on a Beckman DU spectrometer equipped with a Gilford optical density converter. NADH concentrations during reaction were monitored in a 0.1-cm cell at 375 or 385 nm. The molar extinctions coefficients are 1820 and 900 M^{-1} cm^{-1}, respectively. CO_2 evolution kinetics were studied on a Gilson respirometer.

Isotope ratio analysis of CO_2 samples was conducted on a Nuclide Associates RMS 6–60 isotope ratio mass spectrometer. Ratios of m/e 45/44 were measured relative to a laboratory standard. Correction for ^{17}O was made as described previously.[15] Isotope effects were calculated from the mass spectrometer data by published methods.[15]

Isotopic analysis of carbon-4 of malic acid was conducted by isotope-ratio mass-spectrometric analysis of the CO_2 produced by treatment of a purified malate sample with malic enzyme, glutathione reductase, NADPH, and oxidized glutathione, as previously described.[16] This method for analysis of the isotopic composition of malate was checked by separate testing of the procedure used in the isotope effect runs. The results of these checks are consistent with the known composition of the malate used and with the precision of such measurements previously carried out in this laboratory.[16]

Buffer Catalysis of CO_2 Hydration. Each Warburg flask contained 5 mL of HEPES buffer, pH 7.8, with enough KCl to bring the total ionic strength to 0.5. After appropriate temperature equilibration, 100 μL of a 1.0 M $NaHCO_3$ solution was added from the sidearm and the rate of CO_2 evolution was measured for at least 10 min. Three measurements were made at each buffer concentration.

Isotope Effect on Hydration of CO_2. The general outline is shown in Scheme I. A solution of HEPES (final concentration 0.1 M), $MgCl_2$ (5 mM), dithiothreitol (1 mM), and PEP (10 mM) in a 100-mL flask was degassed for 4 h by purging with CO_2-free N_2 at 24 °C. After this, 134 mg of NADH, 1000 units of malate dehydrogenase, and 34 units of PEP carboxylase were added (final volume of solution 50 mL). The CO_2 hydration was initiated by blowing N_2 containing 1% of CO_2 of known isotopic composition over the stirred reaction mixture[17] at a rate such that no depletion of CO_2 in the gas phase occurred. The solution was stirred vigorously throughout the reaction period. Aliquots were withdrawn at various times for measurement of NADH concentration. After all the PEP was consumed, 0.1 mL of concentrated H_2SO_4 was added. After 15 min KOH was added to bring the solution to neutral pH, after which the malate was purified by ion-exchange chromatography on Dowex-1.[16]

Table I. Carbon Isotope Effects on the Hydration of CO_2 at pH 7.5, 24 °C,[a] in Aqueous Solution

isotope ratio[b] m/e 45/44 × 10^6		
carbon-4 of malate	CO_2 tank	k^{12}/k^{13} [c]
11435	11522	1.0065
11427	11522	1.0072
11432	11522	1.0067
11432	11523	1.0068
11427	11523	1.0073
		mean 1.0069 ± 0.0003

[a] Reaction conditions are described in the Experimental Section. [b] Decade settings for isotope ratio m/e 45/44, corrected to a constant value of the reference standard and corrected for the presence of ^{17}O (ref 15). [c] Corrected for the equilibrium isotope effect on the dissolving of CO_2 in H_2O (ref 2 and 3).

Hydration of $^{13}C^{18}O_2$. Five milliliters of a stirred, CO_2-free solution under N_2 containing 0.1 M HEPES, pH 7.5, 10 mM PEP, 5 mM NADH, 5 mM $MgCl_2$, 0.5 mM dithiothreitol, 30 units of malate dehydrogenase, and 10 units of PEP carboxylase was equilibrated to 24 °C. This solution was connected via tubing and a peristaltic pump to a flask containing 2 L of N_2 containing 1% $^{13}C^{18}O_2$. Aliquots were withdrawn at intervals and analyzed spectrophotometrically for NADH. After all the NADH was consumed the remaining solution was acidified by addition of 50 μL of concentrated H_2SO_4. After 10 min the solution was readjusted to pH 8 and then concentrated. D_2O and EDTA were added, and the ^{13}C NMR spectrum was measured. The ^{18}O content was calculated from the integrated intensities of the isotopic satellites in the ^{13}C NMR spectrum.[11]

Isotope Effect on Dehydration of HCO_3^-. Two procedures were used to measure the dehydration isotope effect. In the first procedure, 10 mL of 0.5 M HEPES, pH 8.2, was placed in a 100 mL, three-necked, round-bottom flask equipped with a magnetic stirring bar. This buffer was freed of dissolved CO_2 by purging with CO_2-free He for 4 h. The He gas, on leaving the flask, passed first through a trap immersed in dry ice and then through a second trap. After the degassing was completed, the dehydration was initiated by adding 1.0 mL of 1.0 M $NaHCO_3$ to the solution through a septum and the second trap was cooled with liquid nitrogen. The He purge was continued, and the CO_2 produced in the first 3–6 min of reaction was collected and purified by distillation. The quantity of CO_2 produced was measured manometrically, after which the material was measured by isotope-ratio mass spectrometry. CO_2 samples for 100% conversion were produced by addition of a parallel $NaHCO_3$ solution to a degassed solution of dilute H_2SO_4.

The second procedure utilized the same general equipment setup, except that the system was attached to a high-vacuum line. The solution was degassed with N_2. Reaction was initiated by addition of a $NaHCO_3$ solution as before, following which the second trap was cooled with liquid nitrogen and the system was evacuated through the liquid-nitrogen trap. Vigorous stirring was maintained throughout. The reaction was allowed to proceed for 3–4 min, after which the stopcocks on the CO_2 trap were closed. The CO_2 was then purified and analyzed as described above.

Results

Buffer Catalysis. HEPES Buffer was chosen for study of CO_2 hydration because it does not fit into either of the two broad categories of buffer which have been found to catalyze CO_2 hydration.[14] To confirm this expectation, the rate of dehydration of HCO_3^- was measured at pH 7.8 in the presence of 0.1–0.5 M buffer. Less than a 10% increase in rate was observed in this interval. Thus, buffer catalysis contributes negligibly to the rate in the 0.1 M buffer used in the isotope-effect studies.

CO_2 Hydration Isotope Effect. The carbon isotope effect on the hydration of CO_2 was measured by adding gaseous CO_2 of known isotopic composition to a stirred aqueous solution at pH 7.5 containing PEP, PEP carboxylase, malate dehydrogenase, and NADH (Scheme I). PEP carboxylase requires HCO_3^- and does

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(17) This procedure is advantageous because it provides an appropriate concentration of CO_2 at equilibrium in the aqueous solution and it prevents isotopic depletion of the CO_2 reservoir.

Table II. Carbon Isotope Effects on the Dehydration of HCO_3^- at pH 8.2, 24 °C, in Aqueous Solution

isotope ratio[a] m/e 45/44 × 10^6		
low conversion	high conversion	k^{12}/k^{13} [b]
11256	11407	1.0140
11239	11410	1.0156
11243	11410	1.0152
11254	11405	1.0139
11245	11404	1.0146
	mean	1.0147 ± 0.0007

[a] Decade settings for isotope ratio m/e 45/44, corrected to a constant value of the reference standard. [b] Corrected for percent reaction and for the presence of ^{17}O, but not otherwise corrected.

not react with CO_2.[18] High enzyme concentrations were used so that HCO_3^- would be taken up by PEP carboxylase as rapidly as it was formed and the oxalactate produced would be immediately reduced to malate. This malate was purified by ion-exchange chromatography, after which carbon-4 was converted to CO_2 by use of malic enzyme,[16] and this CO_2 was subjected to isotope-ratio analysis. The isotope effect was calculated by comparison of this isotopic composition with that of the starting CO_2 on the assumption that isotopic equilibrium was maintained between gaseous CO_2 and dissolved CO_2 in the reaction vessel (this isotope effect is 1.0011, with ^{13}C concentrating in the gas phase[2,3]). The data are summarized in Table I.

The adequacy of the above method depends on the irreversibility of CO_2 hydration under the reaction conditions. This irreversibility was tested by conducting the same reaction with highly enriched $^{13}C^{18}O_2$. The ^{18}O content of the malate produced was analyzed by ^{13}C NMR. In the absence of exchange, the ^{18}O content of malate should be two-thirds that of the starting CO_2. This was found to be the case, to within the reproducibility of ±5% expected in the NMR integrations.

Carbon Isotope Effects on the Dehydration of HCO_3^-. This isotope effect was obtained by addition of $NaHCO_3^-$ of known isotopic composition to a buffered solution at pH 8.2. CO_2 was removed from the solution as rapidly as it was formed either by sweeping the solution with He or by conducting the reaction in an evacuated vessel, with CO_2 being continuously trapped in liquid nitrogen. High stirring rates were maintained in order to ensure that CO_2 was removed rapidly from the solution. The isotope effect was calculated by comparison of the isotopic composition of the CO_2 produced at low (ca. 10%) conversion with that produced at 100% conversion. Both CO_2 removal methods gave the same results (Table II). Subsequent studies by an independent investigator using method 2 gave the same isotope effect at 24 °C and an isotope effect at 1 °C that was slightly larger, as expected (k^{12}/k^{13} = 1.0174; P. Paneth, unpublished).

Discussion

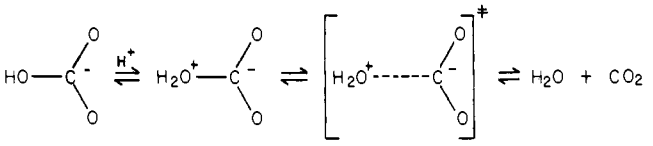
Measurement of the kinetic isotope effect on the hydration of CO_2 is a difficult experimental problem because it is difficult to prevent reversion of HCO_3^- to CO_2. Use of high levels of PEP carboxylase (which uses only HCO_3^- and not CO_2) effectively circumvents this problem. Use of correspondingly high levels of malate dehydrogenase and NADH ensures that oxalacetate does not accumulate but is rapidly and irreversibly converted to malate. Experiments with $^{13}C^{18}O_2$ demonstrate that hydration of CO_2 is effectively irreversible under our reaction conditions. We can calculate from the known isotope fractionations in this system that even if 5% of the HCO_3^- formed were to revert to CO_2, the calculated isotope effect on CO_2 hydration would only be increased from 1.0069 to 1.0074.

We have assumed in our calculation of the isotope effect on CO_2 hydration that isotopic equilibrium between gas-phase CO_2 and dissolved CO_2 is maintained during the course of the experiment. Alternatively, we could assume that CO_2 dissolution is under kinetic control and no isotope fractionation occurs between gas-phase CO_2 and dissolved CO_2. If that were so, then the calculated isotope effect on CO_2 hydration would be 1.0077, only marginally larger than the value calculated previously.

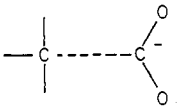
The validity of the isotope effect procedures used here is strengthened by the high reproducibility of the isotope effect measurements, by the similarity of the isotope effects on dehydration of HCO_3^- obtained by two different methods, by the ability of two independent investigators to obtain the same isotope effect in the dehydration reaction, and by the occurrence of the expected temperature dependence of the dehydration isotope effect. Further, the ratio of the HCO_3^- dehydration isotope effect (k^{12}/k^{13} = 1.0147 ± 0.0007) to the CO_2 hydration isotope effect (k^{12}/k^{13} = 1.0069 ± 0.0003) gives a calculated equilibrium isotope effect for CO_2 hydration of 1.007 ± 0.0008, in good agreement with the experimental value of 1.0090 measured by Mook et al.[4,19]

Mechanism. The hydration of CO_2 under the conditions studied here appears to proceed by direct reaction of CO_2 with H_2O,[12,13] and buffer catalysis appears to be unimportant. In the reverse direction, the reaction proceeds with the stoichiometry $H^+ + HCO_3^-$. Although this defines the stoichiometry for the transition state of the reaction, it does not specify a reaction mechanism. Perhaps the simplest mechanism is that shown in Scheme II, in which HCO_3^- reacts first with H^+ to form a zwitterion, which decomposes unimolecularly.

Scheme II



Carbon isotope effects have been measured for a variety of carboxylations[8] and decarboxylations,[6,7] reactions in which CO_2 is a reactant or product and a bond is made or broken to another carbon atom. Transition states for such processes are generally similar to that suggested above for CO_2 hydration/dehydration:



Carbon isotope effects for such transition states are generally in the range 1.03–1.07 when the carbon–carbon bond-making or -breaking process is entirely rate limiting.[6-8] Carbon isotope effects for addition of nucleophiles to the carbonyl group of methyl benzoate are in this same range.[21] Provided that replacement of carbon by oxygen makes no more than a small difference, these isotope effects should provide a proper standard for predicting the carbon isotope effect on CO_2 hydration. By these comparisons, the isotope effects observed for CO_2/HCO_3^- interconversion are surprisingly small.

Carbon isotope effects in decarboxylations are generally believed to increase in size as the transition state becomes more product-like. By this argument, the small isotope effect in HCO_3^- dehydration indicates that the transition state is much earlier than corresponding transition states in decarboxylation processes; that is, the transition state must resemble HCO_3^-, rather than CO_2. This is reasonable, from the point of view that the zwitterionic intermediate in Scheme II is of very high energy, and we would expect that the transition state would resemble this intermediate.

Although it is not possible at this point to eliminate convincingly the mechanism in Scheme II, this mechanism must be considered

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(19) The measurement of Mook et al.[4] gave an isotope effect K^{12}/K^{13} = 1.0079 at 25 °C for the equilibrium isotope fractionation between gaseous CO_2 and dissolved HCO_3^-. When this value is combined with the equilibrium isotope effect for dissolving CO_2 in water (K^{12}/K^{13} = 1.0011, with ^{13}C concentrating in the gas phase[2,3]), the equilibrium isotope effect between dissolved CO_2 and dissolved HCO_3^- becomes 1.0090. Note that the isotope effect on dissolution of CO_2 was erroneously given the wrong sign in an earlier publication from this laboratory.[20]

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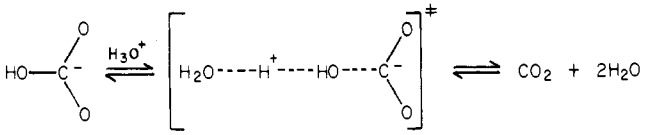
Scheme III



questionable, for the following reason: the rate constant for unimolecular decomposition of H_2CO_3 is 18 s^{-1} (ref 13). This rate constant is related to Scheme II by the equilibrium constant for the interconversion

$$H_2CO_3 \rightleftharpoons H_2O^+\text{–}CO_2^-$$

If this equilibrium constant is about 10^{-8}, then the actual rate constant for decomposition of the zwitterion in Scheme II is about 10^9 s^{-1}, which is near the diffusion-controlled limit; if the equilibrium constant is less than this value (as might easily be the case), then the mechanism of Scheme II is impossible because the required rate of decomposition of the zwitterionic intermediate exceeds the diffusion-controlled limit.

The solvent isotope effect on the dehydration of HCO_3^- ($k_{H_3O^+}/k_{D_3O^+} = 0.56$) is similar in magnitude to solvent isotope effects observed in A-1 type cleavages in which the transition state is product-like.[13] However, if the mechanism shown in Scheme II is correct, then carbon isotope effects indicate that the transition state must be reactant-like, and this should give a solvent isotope effect near unity. Thus, it appears that the mechanism shown in Scheme II is not correct.

The alternative to the specific-acid-catalyzed mechanism of Scheme II is a general-acid-catalyzed mechanism, as suggested by Pocker and Bjorquist[13] (Scheme III), in which H_3O^+ serves as a general acid and H^+ transfer is concerted with C–O bond breaking. Again, the carbon isotope effect indicates an early transition state. The solvent isotope effects, small salt also consistent with such a scheme. This mechanism also avoids the diffusion-control problem which occurs with Scheme II. The carbon and solvent isotope effect studies, taken together, appear to favor this mechanism over that shown in Scheme II.

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Registry No. ^{13}C, 14762-74-4; CO_2, 124-38-9; HCO_3^-, 71-52-3.

Effect of Free Energy on Rates of Electron Transfer between Molecules[1]

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Abstract: Rates of electron-transfer (ET) reactions $D^- + A \rightarrow D + A^-$ between aromatic molecules in a rigid organic solid have been measured from 10^{-7} to 10^2 s following creation of radical anions by pulse radiolysis. By avoiding the problems of diffusion control and complexing between the donor and acceptor which occur in liquids, these data provide the first opportunity to interpret measurements of electron-transfer rates vs. exothermicity with ET theories. Reactions having free energy changes from $-\Delta G° = 0.01$ to 2.75 eV were studied. For each reaction, the ET rate constant $k(r)$ is quantitatively measured as a function of distance using the random distribution of distances between D^-, A pairs. The ET rates are very slow for weakly exothermic reactions, are maximized at an intermediate exothermicity λ, and decrease at high exothermicity. λ is observed to increase gradually with time, due apparently to solvent relaxation around D^- ions suddenly formed in the rigid medium. Because this causes the distance dependence of the rates to vary with exothermicity, quantitative comparison of the data with ET theories is possible only if we assume that the distance dependence of electron exchange interactions does not depend on the acceptor. This assumption, which is consistent with elementary theories of electron exchange interactions, allows the following conclusion to be drawn from the data: (1) The rate vs. energy relation at a given time can be described by standard ET theories which consider reorganization of both low-frequency solvent modes and high-frequency molecular vibrations. (2) An empirical dependence of the solvent reorganization energy (λ_s) on time, obtained from the shift of the peak of the rate vs. $\Delta G°$ curve, gives good account of the shapes of the kinetic decay curves but underestimates the rates for highly exothermic reactions. (3) No information is obtained about the effect of molecular orientation, but the orientation-averaged rates may be extrapolated to shorter distances to estimate a rate of $10^{13.3}$ s^{-1} for optimally exothermic ET between species in contact at 296 K. (4) Because this contact rate is more than 2 orders of magnitude larger than necessary for diffusion control, the rate constants for diffusional ET reactions in fluids are expected to provide little information about dependence of rates on exothermicity. (5) The rates decrease exponentially with distance $k(r) = \nu \exp(-r/a)$ with $a = 0.83$ Å.

1. Introduction

A. Background on Energy vs. Electron-Transfer Rates. Theories of electron-transfer (ET) processes in condensed media[2-21] have consistently predicted a relationship between kinetics and thermodynamics: Rates are expected to be slow for weakly exothermic

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