

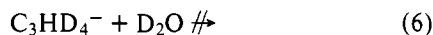
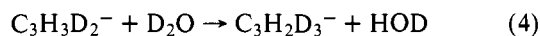
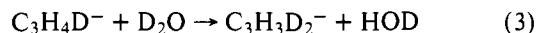
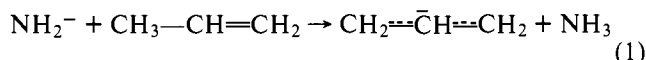
Hydrogen–Deuterium Exchange Reactions of Carbanions with D₂O in the Gas Phase

John H. Stewart, R. H. Shapiro,* C. H. DePuy,*
and Veronica M. Bierbaum

*Contribution from the Department of Chemistry, University of Colorado,
Boulder, Colorado 80309. Received April 4, 1977*

Abstract: Using the flowing afterglow technique, we have observed that carbanions participate in sequential deuterium exchange reactions with D₂O in the gas phase. The extent of exchange is reported for 32 carbanions and the mechanism of the reaction is discussed. The usefulness of this phenomenon as a probe of the acidity and structure of anions is described.

Many organic anions are readily prepared in the gas phase by proton abstraction from organic neutrals with strong bases such as OH⁻ and NH₂⁻. The subsequent reactions of these carbanions constitute a fertile but relatively unexplored area of study. In our flowing afterglow studies of carbanions we have observed, rather unexpectedly, that many organic anions undergo facile hydrogen–deuterium exchange reactions with deuterium oxide.¹ For example the allyl anion, generated from propylene by proton abstraction, undergoes sequential replacement of deuterium for hydrogen to form more highly deuterated anions (eq 1–6). In contrast to solution exchange processes, the gas phase exchange must occur in an intermediate reaction complex. The interesting mechanistic implications of this process will be discussed, including apparent D₂O-catalyzed isomerizations of the anion.



We have observed varying extents of reactions of organic anions with D₂O, including complete exchange of all available hydrogens, intermediate degree of exchange, as well as no exchange whatever. Therefore in the same way that proton abstraction from a neutral examines the acidity of that neutral, the exchange reactions of anions with D₂O serve as a sensitive probe of the acidities of the hydrogen atoms in the anion. Even more importantly, the exchange process promises to be of value as a diagnostic tool for the determination of the structure of an ion as well as for distinguishing among isomeric ions.

These negative ion–D₂O exchange reactions are the anionic analogue of the carbon cation–D₂O exchange processes reported by Beauchamp and co-workers² and by Martinsen and Buttrill.³

Experimental Section

Our experiments were performed with a flowing afterglow system⁴ which has been described in detail previously.⁵ The reaction vessel is a 100 cm × 7.6 cm i.d. stainless steel cylinder through which helium buffer gas flows at pressures near 0.5 Torr and velocities of ~10⁴ cm s⁻¹. At the upstream end of the reaction tube the precursor ions, NH₂⁻ or OH⁻, are generated by addition of small flows of other gases past the ionizer. NH₂⁻ is produced by dissociative electron attachment to NH₃. OH⁻ is formed by electron impact on N₂O to give O⁻ followed by rapid hydrogen atom abstraction from CH₄. In the next 30 cm the plasma develops well-defined diffusion and flow characteristics and the ions are thermalized by greater than 10 000 collisions with helium.

The neutral organic molecules are then introduced to the thermalized plasma and their anions are generated by proton abstraction by NH₂⁻ or OH⁻. Finally, the D₂O reactant is added in the last 15 to 55 cm of the system. Most of the reaction mixture is exhausted by the pumping system, but a small fraction of the ions is sampled, analyzed with a quadrupole mass filter, and detected with an electron multiplier.

For these experiments the helium flow rate and density were 120 atm cm³ s⁻¹ and 8.3 × 10¹⁵ cm⁻³, respectively. The D₂O concentration ranged from about 1 × 10¹¹ to 2 × 10¹³ cm⁻³ and densities of the organic neutral were generally ~1 × 10¹² cm⁻³. Ion densities ranged from 10⁵ to 10⁸ cm⁻³. For a buffer gas velocity of 8 × 10³ cm s⁻¹, the time available for exchange is ~2 to 7 ms. All experiments were performed at room temperature.

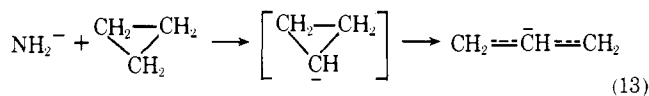
Gas purities were as follows: helium (99.995%), ammonia (99.999%), methane (99.0%), and nitrous oxide (98.0%). Deuterium oxide had a minimum isotopic purity of 99.7%. Most organic reactants were obtained from commercial suppliers and used without further purification. Liquid reactants without acidic hydrogens were distilled directly into the reaction system from lithium aluminum hydride or calcium hydride to eliminate water contamination. The deuterated compounds CH₃C≡CD, CH₃CH₂C≡CD, CD₃CHO and CH₂=CHCH₂OD were synthesized using published techniques.

Results and Discussion

Table I summarizes the extent of hydrogen–deuterium exchange exhibited by 32 organic anions. Note the wide variety of structural types of anions which undergo exchange. We will discuss several of these types in turn.

Alkenes. In the allyl anion only four of the five hydrogens are susceptible to replacement by deuterium, with the unique vinyl hydrogen not participating in exchange. A similar result has been found in solution.⁶ The result is in accord with the observation that hydroxide ion is not sufficiently basic to remove a proton from ethylene⁷ and only allylic protons can be abstracted. However, all seven of the hydrogens of the various isomeric butene anions (C₄H₇⁻) are exchangeable as are all hydrogens in the anions from 1-pentene (C₅H₉⁻) and from 1-hexene (C₆H₁₁⁻). An exchange mechanism consistent with these data involves formation of a reaction intermediate between the anion and D₂O, in which deuteration of the anion occurs, followed by proton abstraction by the OD⁻. The deuterated organic anion and HOD then separate (reaction 7). The monodeuterated anion may then encounter another D₂O molecule and repeat the process. By appropriate protonations at either end of the delocalized anionic system all protons in the butenyl anion will become allylic at one time or another and so be exchangeable. This is not the case for the allyl anion in which the central proton can never become allylic. Some of the reaction intermediates represented in eq 7 may have sufficiently long lifetimes to allow exchange of both deuterium atoms before dissociation of the complex.

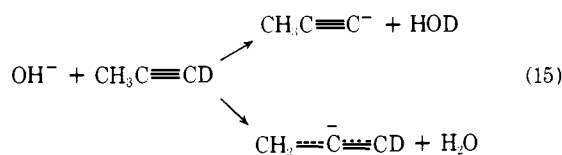
A second possible mechanism involves a concerted exchange process. Donation of a deuteron by D₂O to the carbanion with simultaneous abstraction of a proton from the same carbon or



Allenes and Alkynes. Allene readily reacts with NH_2^- or OH^- to give an anion of *m/e* 39⁷ (eq 14).



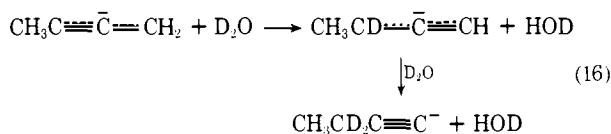
Upon reaction with D_2O , all three hydrogens in the anion can be replaced by deuterium. Surprisingly, all three hydrogens in the anion produced by proton abstraction from propyne ($\text{CH}_3\text{C}\equiv\text{CH}$), an isomer of allene, are also exchangeable. This unexpected result suggests that in propyne, at least some proton abstraction from the methyl group must occur. To test the relative kinetic acidities of the two types of hydrogens in propyne, we prepared the 1-deuterio analogue by exchange with aqueous $\text{D}_2\text{O}/\text{OD}^-$. When this monodeuterated hydrocarbon was converted to its anion in the gas phase by reaction with OH^- , abstraction occurred from both the acetylene and methyl moieties (eq 15). This striking enhancement in gas phase



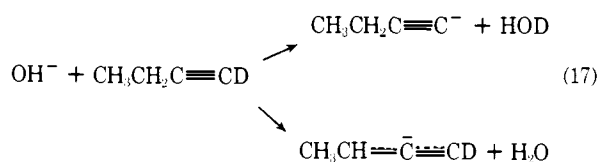
acidity of the methyl hydrogens relative to solution presumably arises from the resulting delocalization of charge through the indicated resonance structure since charge dispersal through solvating ligands is not possible.¹⁰

It should be stressed that the formation of the C_3D_3^- anion on a time scale of milliseconds in our flowing afterglow system must be a gas phase ion-molecule reaction since we have not observed the corresponding reaction in solution ($\text{CH}_3\text{C}\equiv\text{CH}/\text{D}_2\text{O}/\text{OD}^-$) even after a period of many days.

The anion formed by proton abstraction of 2-butyne exchanges only two of its five hydrogens. This result can be explained in terms of water-catalyzed isomerizations of the anion (eq 16). The anion of 1-butyne similarly exhibits hydrogen-



deuterium exchange of only two hydrogens. Gas phase proton abstraction studies of the deuterium labeled 1-butyne confirm that both alkyl and acetylene protons are removed (eq 17). We



are currently studying the position of proton abstraction from substituted acetylenes using a variety of anionic bases and will report the results in a later publication. Finally, the anion generated from neutral 1,2-butadiene ($\text{CH}_3\text{CH}=\text{C}=\text{CH}_2$) also exhibits only two exchanges. Therefore it may be concluded that in the gas phase allenic and acetylenic hydrogens have comparable acidities and may be interconverted through reaction with water.

The anion of the same *m/e* 53 formed by proton abstraction from 1,3-butadiene is a stronger base than OD^- . This organic ion may therefore be distinguished from the isomeric anions of 1-butyne, 2-butyne and 1,2-butadiene in that it reacts with D_2O primarily by deuterium abstraction, forming OD^- .

The unsubstituted acetylide anion (C_2H^-), formed by the reaction of hydroxide with acetylene, does not exchange with D_2O .

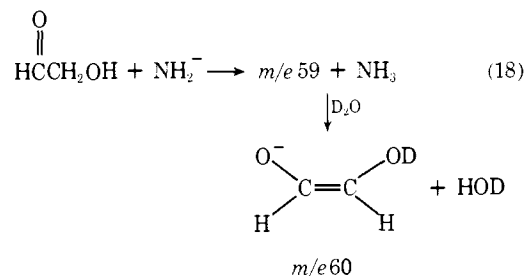
Enolate Ions. In general we find that enolate anions derived from aldehydes and ketones do not participate in hydrogen-deuterium exchange reactions with D_2O . For example, the anion of *m/e* 57 ($\text{CH}_3\text{COCH}_2^-$) formed from acetone does not exchange with D_2O nor does the anion of *m/e* 43 ($^-\text{CH}_2\text{CHO}$) from acetaldehyde. In the latter example deuterium labeling has confirmed the position of abstraction.

Alkoxide Ions. Alkoxide ions, for example CH_3O^- , do not exchange with D_2O . Rather, localization of the charge on the electronegative oxygen atom enhances the formation of hydrogen-bonded clusters, e.g., $\text{CH}_3\text{O}^-(\text{D}_2\text{O})$. Proton abstraction from allyl alcohol produces an anion which clusters rather than exchanges with D_2O . This suggests that in analogy with solution studies the alkoxy proton is preferentially abstracted even though removal of the α proton would form a resonance stabilized ion. This hypothesis was supported by proton abstraction experiments of the deuterated species $\text{CH}_2\text{CHCH}_2\text{OD}$.

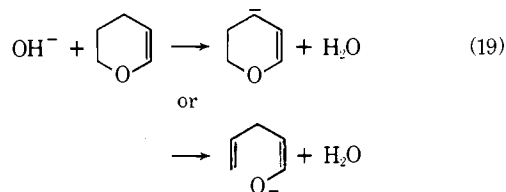
The butoxide ($\text{C}_4\text{H}_9\text{O}^-$, *m/e* 73) and pentoxide ($\text{C}_5\text{H}_{11}\text{O}^-$, *m/e* 87) anions which do not exchange with D_2O can be readily distinguished from the ester anions $^-\text{CH}_2\text{COOCH}_3$ (*m/e* 73) and $^-\text{CH}_2\text{COOCH}_2\text{CH}_3$ (*m/e* 87) which exhibit two exchanges.

Other Anions. As can be seen from Table I, other pairs of anions with the same mass to charge ratio can be distinguished from one another by this exchange technique.

The acetate anion generated by proton abstraction from acetic acid does not exchange with D_2O . However, the isomeric anion formed from glycol aldehyde exhibits a single exchange reaction (eq 18).



Proton abstraction from dihydropyran and from 1-hexene produce anions of the same mass which can be distinguished by their exchange reactions with D_2O . The hexene anion exchanges all 11 hydrogens while the anion of dihydropyran exhibits no exchange with D_2O . This fact allows a reasonable choice between two possible structures of the dihydropyran anion. Proton abstraction from dihydropyran would give an allyl anion while β -elimination would produce an enolate ion (eq 19). Since the *m/e* 83 ion does not undergo exchange with



D_2O , the enolate structure is strongly favored for this ion.

The benzyl anion formed by proton abstraction from toluene exchanges only two hydrogens. The apparent basicity of the ring hydrogens relative to water is consistent with the observation that the phenyl anion reacts with D_2O by deuterium abstraction. The anion of cycloheptatriene should either exhibit no exchange or complete exchange with D_2O and thus be distinguishable from the isomeric benzyl ion. However, we have

not yet succeeded in unequivocally producing this anion in our system.

The bicarbonate anion was produced by the addition reaction of OH^- with CO_2 . Downstream addition of D_2O converted the HCO_3^- ion to its deuterated form. For this experiment, it was essential to form the anion in the absence of H_2CO_3 since heterogeneous exchange with D_2O might be proposed as a complicating factor.

It is interesting to compare the D_2O reactions for the anions $^- \text{CH}_2\text{NO}_2$, $^- \text{CH}_2\text{COOCH}_3$, and $^- \text{CH}_2\text{CN}$ which have been generated by proton abstraction from a methyl group. The anion from nitromethane exhibits no exchange, only clustering with D_2O . For the anion of methyl acetate exchange and clustering appear as competitive reactions while for the anion of acetonitrile, exchange reactions dominate. This trend from cluster to exchange reactions reflects the increasing basicity of the anions or, correspondingly, the decreasing acidity of their parent neutrals.

The phenomenon of hydrogen-deuterium exchange promises to have as important applications in the gas phase as in solution. It serves as a probe of the acidity of anions and frequently assists in assigning ion structures or in distinguishing between ions of the same mass. The mechanistic questions are intriguing and their full resolution would make fundamental contributions to our understanding of ion-neutral encounters.

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References and Notes

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- (10) In a typical experiment ~60% of the ions contained a deuterium atom, indicating that at least 60% of proton removal occurred from the methyl group. As a referee has pointed out, this represents a minimum value; hydrogen-deuterium exchange could occur in the delocalized ion-water complex resulting in deuterium loss even if initial proton abstraction occurs from the methyl group.

The Effect of Solvation on Brønsted β Values for Proton Transfer Reactions

D. J. Hupe* and Dorothy Wu

Contribution from the Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109. Received February 18, 1977

Abstract: The rates of reaction of **1** with 30 oxyanion bases in aqueous solution at 25 °C are reported. The data produce a Brønsted plot for the rate-determining enolization reaction which is definitely curved. Hydroxide ion is not anomalous but behaves like other highly basic oxyanions. Anions of hydrogen peroxide and oximes show no α effect and behave like other oxyanions of the same basicity. The cause of the curvature in the Brønsted plot is considered. A Hammond postulate argument consistent with a considerable change in transition state structure with changing catalyst $\text{p}K_a$ is contrasted with an argument based on the effects of transition state solvation. These arguments are expressed in terms of the Marcus proton transfer theory and the solvation argument is favored. Literature data are compared with that for **1**, and it is shown that two effects determine the slope of a Brønsted plot for proton abstraction from carbon. A gradual change in slope, reflecting changes in transition state bond order, is observable only over a very large change in $\Delta\text{p}K_a$ and cannot be perceived with the single substrate and homologous set of catalysts typically found in a Brønsted plot. We conclude that perturbation due to solvation of the bases involved is responsible for Brønsted plot curvature. This effect is a function only of the catalyst $\text{p}K_a$, is independent of the substrate used, and causes an increase in β for low $\text{p}K_a$ catalysts and a decrease in β for high $\text{p}K_a$ catalysts. Mechanistic ramifications of this proposed explanation are discussed.

Brønsted plots for proton transfer from carbon have been interpreted in two distinct ways. One may pass a straight line through a series of points for bases such as amines or acetates with the result that hydroxide ion falls anomalously below the line.^{1,2} This straight line implies little change in transition state structure with the change in catalyst basicity. Alternatively, one may draw a curved line through the data points (including hydroxide ion) which implies a rapid change in transition state structure with changing catalyst basicity.^{3,4} In this study, we present the rates obtained for the enolization of substrate **1** which includes data on a wide variety of oxyanions such as highly basic alkoxides, phenoxides, and oxime anions. The

Scheme I

