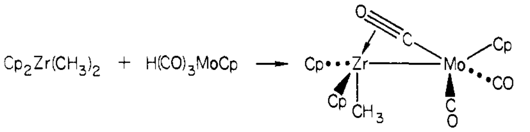
occupation. This is also illustrated in Table II, which lists the Mulliken populations in the orbitals for both kinds of CO ligands. The increase in occupancy of the π^* orbitals ($2\pi_{\|}$ and $2\pi_{\perp}$)[16] is due primarily to an increased bonding interaction of these orbitals with the Mo orbitals. The overlap populations (0.17 for terminal, 0.25 for bridging CO) reflect this increased π^* backbonding. In the case of the titanium atom, however, metal to π^* backbonding is negligable. The 4σ orbital is the highest σ orbital with significant oxygen character. In fact, it is almost entirely oxygen lone pair in character. This orbital is mainly responsible for the titanium–CO bond (overlap population = 0.12), although the 5σ orbital (overlap population = 0.04) and the $1\pi_{\|}$ orbital (overlap population = 0.03) make some contribution. It will be noted in Table II that the 4σ occupancy is less in the bridging than in the terminal carbonyl. The smaller occupancy of this orbital in the bridging carbonyl is consistent with the proposed 4+ oxidation state of the titanium atom, since the oxygen lone pair should be strongly attracted by a large charge nearby. The sizable difference between the Mulliken gross atomic charges (0.90 for Ti, 0.36 for Mo) also concurs with this assignment of the oxidation state. The $1\pi_{\|}$ orbital of the bridging carbonyl lies in the mirror plane and acts as a σ donor orbital to empty Ti orbitals in the same plane. Since one of these empty orbitals bisects the angle between the methyl and carbonyl ligands, more effective overlap is achieved by bending the CO ligand toward this orbital (Ti–O_1–C_1 = 144.3 (3)°, see Figure 1). The $1\pi_{\perp}$–titanium orbital interaction is negligible since there are no nearby titanium acceptor orbitals of appropriate symmetry.[17]

The formation of a Lewis acid adduct between $Cp'_2Ti(CH_3)$ and $(OC)_3MoCp$ indicates such structures may be observed in other systems. In particular, such an adduct may be important in the recently reported dinuclear elimination reaction of $Cp_2Zr(CH_3)_2$ and $H(CO)_3MoCp$[18] (reaction 1). The proposed



(1)

1

structure of **1** is based on IR and ^{13}C NMR data. The IR spectrum shows a strong band at 1545 cm^{-1} which is assigned to the bridging carbonyl ligand shown in (1). The ^{13}C NMR spectrum at room temperature has a single carbonyl peak at δ 236.1, while two peaks at δ 245.4 and 232.5 (relative intensity 1:2) are observed when the spectrum is recorded at −80 °C. We propose that a Zr Lewis acid adduct[19] analogous to the Ti adduct reported in this paper is also consistent with these data. In view of this possibility a crystallographic investigation of the Zr system would be of interest.

Finally, this reaction demonstrates a novel method of generating an open coordination site on a transition-metal complex. Further studies to extend the scope of this reaction to other transition-metal hydrides and carbenes, as well as studies on the reactivity of the Ti–Mo system, are under way.

Acknowledgment. The support of the National Science Foundation under Grant NSF-CHE-78-16-7724964 is gratefully acknowledged.

Supplementary Material Available: A listing of positional and thermal parameters derived from full-matrix least-squares refinements (5 pages). Ordering information is given on any current masthead page.

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[16] C_s symmetry was imposed on the molecule so that the C(methyl), Ti, O_1, C_1, and Mo atoms lie in a mirror plane along with the centroid of the molybdenum cyclopentadienyl ring. The 2p atomic orbitals which form the basis for $1\pi_{\|}$ and $2\pi_{\|}$ are parallel to the mirror plane; those for $1\pi_{\perp}$ and $2\pi_{\perp}$ are perpendicular to the aforementioned 2p orbitals and the C–O internuclear axis.

[17] An interesting comparison was made with a system in which the $Cp_2Ti(CH_3)$ moiety used in the calculations was replaced with a group having no d orbitals, viz., the H_3O^+ ion. The H_3O^+ oxygen and one of its hydrogen atoms were oriented collinearly with the C–O ligand axis, giving distances of 1.579 and 2.59 Å, respectively, from the hydrogen and oxygen atoms to the carbonyl oxygen. The negative charge on the CO oxygen atom increased substantially (from −0.11 to −0.35), and the C–O bond strength increased slightly, as measured by overlap populations (from 0.59 to 0.62).

[18] Longato, B.; Norton, J. R.; Huffman, J. C.; Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 209.

[19] A zirconium Lewis acid adduct has been proposed as an intermediate in reactions of the type $L_nMCO + H_2ZrCp'_2$: Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121.

Gas-Phase Hydrogen–Deuterium Exchange Reactions in Carbanions: Exchange of Vinyl and Aryl Protons by D_2O

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Received November 19, 1980

In previous papers[1,2] we showed how gas-phase hydrogen–deuterium exchange reactions between carbanions and deuterated reagents such as D_2O, CH_3OD, and CF_3CH_2OD can be used to determine ion structures, bracket carbanion basicities, and probe ion-molecule reaction mechanisms. Hunt and Sethi recently demonstrated the utility of H–D exchange in negative chemical ionization mass spectrometry (NCIMS) in which the number of hydrogen atoms of various types can be counted directly in a mass spectrometer.[3] Using ion cyclotron resonance spectroscopy, Nibbering and co-workers have applied H–D exchange to the solution of a variety of ion structural problems.[4] In view of the large number of potential applications of gas-phase H–D exchange, it is important to understand the full range of its utility as well as its possible pitfalls. We wish to report that under the proper conditions D_2O can serve as an exchange reagent for hydrogens which are much less acidic than water; as a result, in certain carbanions aryl and vinyl hydrogens can be observed to exchange with D_2O. Such exchanges give rise to many new possible applications for the technique, especially as a tool for investigating relative acidities of types of hydrogens which have not been previously studied. At the same time, they may add unexpected complications to the routine use of the technique with NCIMS.

Using our flowing afterglow apparatus,[5] we have previously examined the exchange characteristics of a wide variety of organic anions. Three types of behavior were delineated, depending upon the base strength of the carbanion relative to that of the conjugate base of the exchange reagent. These are illustrated below for reactions with D_2O and are as follows: proton transfer for anions which are stronger bases than OD^- (eq 1), H–D exchange for

$$\underset{(398)}{C_6H_5^-} \xrightarrow{D_2O} \underset{(391)}{OD^-} \tag{1}$$

$$\underset{(372)}{\overset{-}{C}H_2CN} \xrightarrow{D_2O} \overset{-}{C}D_2CN \tag{2}$$

$$\underset{(369)}{\overset{-}{C}H_2COCH_3} \xrightarrow{D_2O} \text{no exchange} \tag{3}$$

carbanions which are up to about 20 kcal/mol less basic than OD^- (eq 2), and no observable exchange for still weaker bases (eq 3) [proton affinities (PA), in kcal/mol, shown in parentheses].[6] By

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[1] Stewart, J. H.; Shapiro, R. H.; DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1977**, *99*, 7650–7653.

[2] DePuy, C. H.; Bierbaum, V. M.; King, G. K.; Shapiro, R. H. *J. Am. Chem. Soc.* **1978**, *100*, 2921–2922.

[3] Hunt, D. F.; Sethi, S. K. *J. Am. Chem. Soc.* **1980**, *102*, 6953–6963.

[4] (a) Dawson, J. H. J.; Kaandorp, Th. A. M.; Nibbering, N. M. M. *Org. Mass Spectrom.* **1977**, *12*, 330–333. (b) Noest, A. J.; Nibbering, N. M. M. *J. Am. Chem. Soc.* **1980**, *102*, 6427–6429.

[5] Bierbaum, V. M.; DePuy, C. H.; Shapiro, R. H.; Stewart, J. H. *J. Am. Chem. Soc.* **1976**, *98*, 4229–4235.

[6] Bartmess, J. E.; McIver, R. T., Jr. in "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, Chapter 11.

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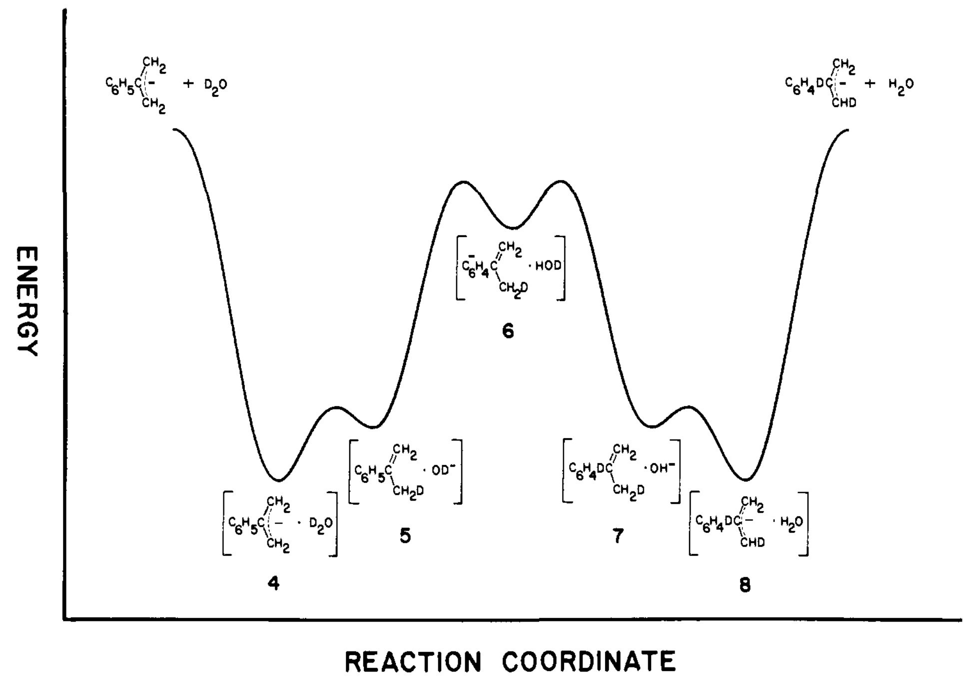


Figure 1. Reaction coordinate for two H-D exchanges in the 2-phenylallyl anion resulting from a single encounter with D_2O.

proper choice of the reagent, exchange can be observed with most carbanions. For example, phenide ion will exchange with ND_3 [$PA(NH_2^-) = 404$], acetone enolate with CH_3OD [$PA(CH_3O^-) = 379$], and nitromethane anion [$PA(CH_2NO_2^-) = 359$] with CF_3CH_2OD [$PA(CF_3CH_2O^-) = 364$].

Our view of the mechanism of the exchange reaction is summarized in eq 4.[1] In the gas phase, an ion and a neutral molecule

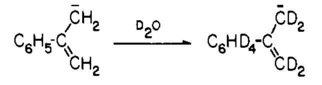
$$R_2\bar{C}H + D_2O \rightleftharpoons \underset{1}{\begin{bmatrix} R_2\bar{C}H \\ D_2O \end{bmatrix}} \rightleftharpoons \underset{2}{\begin{bmatrix} R_2CHD \\ OD^- \end{bmatrix}} \rightleftharpoons \underset{3}{\begin{bmatrix} R_2\bar{C}D \\ HOD \end{bmatrix}} \rightleftharpoons R_2\bar{C}D + HOD \quad (4)$$

are attracted to one another by ion–dipole and ion-induced dipole forces. These forces can amount to 10–20 kcal/mol or more by the time the ion and neutral reach reaction distance and enter into a relatively long-lived ion–molecule complex **1**.[7] The same amount of energy is required to separate the complex into the reactant ion and neutral. Some or all of the excess internal energy contained in the complex can be utilized to carry out an endothermic deuteron transfer to form **2**. However, the OD^- and organic neutral which result now have insufficient energy to separate. Subsequent exothermic proton transfer to OD^- results in exchange as well as a new complex **3** capable of dissociation.

It is also possible to reverse the experiment and use a deuterated organic molecule as an exchange agent for the hydrogen of hydroxide ion:

$$OH^- \xrightarrow{C_6D_6} OD^- \quad (5)$$

Although such an experiment does not reveal anything about the structure of the organic species, it shows that OH^- is also capable of a highly endothermic proton transfer within an ion–dipole complex. If, however, one combines in the same molecule hydrogens which are slightly more acidic than those in water with hydrogens which are less acidic, it becomes possible to generate a carbanion which is not neutralized by D_2O and in which both types of hydrogens exchange. For example, in the 2-phenylallyl anion we have been able to exchange not only the four allylic hydrogens but at least four of the five aryl hydrogens as well (eq 6). The key to the observation of this exchange is that the relative acidity of the two types of C–H bonds must be less than the ion–dipole energy of the initially formed complex (10–20 kcal/mol). This process is illustrated in Figure 1.



(6)

Table I. Extent of Hydrogen-Deuterium Exchange of Carbanions with D_2O

neutral (HA) producing anion (A^-)	no. of H atoms in A^-	maximum no. of H-D exchanges obsd
$CH_2{=}C(CH_3)CH{=}CH_2$	7	7
$C_6H_5C(CH_3){=}CH_2$	9	8
$C_6H_5CH{=}CH_2$	7	7
2-methylene-5-norbornene	9	7
C_6H_5F	4	4
$C_6H_5CF_3$	4	4
$CH_2{=}CHCN$	2	2
$(CH_3)_3CC(CH_3){=}CH_2$	13	4

The initially formed ion–molecule complex **4** has up to 20 kcal/mol of excess energy. Part of this (say 3 kcal/mol)[8] is utilized in the endothermic deuteron transfer to form **5**. An endothermic proton transfer to OD^- of up to 17 kcal/mol is still possible to form **6**.[9] Separation of the complex is only possible when all of the necessary internal energy is regained via **7** and **8**. It is apparent that this mechanism requires an exchange agent possessing at least two deuteriums in order for exchange at the less acidic sites to be observable.

As Table I shows, D_2O is capable of exchanging many types of hydrogens which are less acidic than those in water. These results obviously present a complication with regard to the specificity of H-D exchange. At the same time they offer useful new applications of the technique, since in many cases protons of different types can be distinguished by their relative rates of

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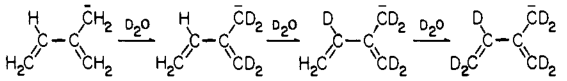
(7) Kebarle, P. *Annu. Rev. Phys. Chem.* **1977**, *28*, 445–476.

(8) We note that energy differences among the various intermediates within the ion–dipole complexes may differ from those measured for the isolated species. Because of the lack of adequate data for estimating these differential solvation energies, we have constructed our model around the simple differences in proton affinities.

(9) The actual limits of the endothermic proton transfers will be determined by the barrier heights separating the intermediate complexes rather than their absolute energies. However, quantitative information concerning the magnitudes of energy barriers for proton transfers is not presently available. (See, however, Jasinski, J. M.; Brauman, J. I. *J. Am. Chem. Soc.* **1980**, *102*, 2906–2913.)

exchange. For example, in the isoprene anion the four allylic hydrogens exchange most rapidly ($k = 9 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}). A fifth proton, which we formulate as that in the 3 position, exchanges more slowly but at a rate which is similar enough to that of the first four to prevent a reliable dissection of its intrinsic exchange rate constant. The final two hydrogens exchange more slowly still with an estimated rate constant of 1×10^{-11} cm^3 molecule^{-1} s^{-1} (eq 7).[10] Thus, by determining not only the



(7)

maximum number of exchangeable hydrogens but also their relative ease of exchange, we can gain important information about the structure of the carbanion. Further, in bracketing hydrocarbon acidities the presence or absence of multiple exchanges may serve to fix an upper or lower limit for certain types of hydrogens in the molecule. For instance, we have found that in the 2-*tert*-butylallyl anion only the four allylic hydrogens exchange with D_2O.

We are presently examining the potential of other compounds for use as exchange agents in different hydrocarbon acidity ranges. The details of our efforts in this area shall appear in a forthcoming publication.

Acknowledgment. We are grateful to the National Science Foundation for financial support under Grant CHE79-09750.

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[10] We do not mean to imply by eq 7 that complete exchange of one type of hydrogen occurs before the other exchange begins but rather that differences in exchange rates can be seen in the mass spectrum.

Dication Ethers (R^+–O–R^+), Conjugated Cations with Remarkably Low Rotation Barriers. A Theoretical Investigation

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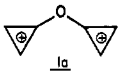
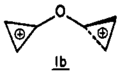
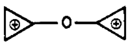
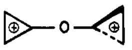
Stang and co-workers[1] recently reported the preparation of novel dication ether salts, $R^+\text{–O–}R^+\cdot 2CF_3SO_3^-$, where R was cyclopropenylium, tropenylium, pyridinium, etc. These novel carbenium ions raise a number of intriguing questions regarding their structures, preferred conformations, rotation barriers, stabilities, and charge distributions. Experimental difficulties have so far frustrated the attempts to answer these questions.[1] This information can be obtained computationally by the application of reliable molecular orbital methods.[2,3] Thus we were prompted to study these species theoretically with both semiempirical and ab initio methods, and in this communication we report the results of these calculations for two dications, dicyclopropenylium ether (**1**) and ditropenylium ether (**2**), both synthesized by Stang.[1]

The dications **1** and **2** were calculated in both planar (**1a**, **1c**, **2a**) and perpendicular (**1b**, **1d**, **2b**) conformations. For **1**, calculations were carried out with both the semiempirical MINDO/3 method[4] and standard ab initio methods.[5] For the larger **2** only MINDO/3 was used. Each structure was fully optimized by using MINDO/3 (for **1** and **2**) and the minimal STO-3G[6a] basis set (for **1**).[7] For **1**, single point calculations with the extended 4-31G basis set[6b] at the optimized STO-3G geometries followed. For comparison, we have carried out similar calculations for the parent ether dication $^+CH_2OCH_2^+$ (**3**) and the hydroxycyclopropenium cation (**4**). The total and relative energies of **1**–**4** are given in Table I.


1a


1b


1c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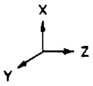
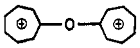
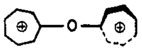
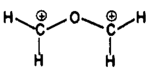
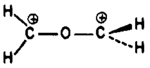
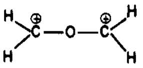


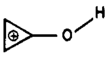

2a

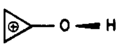

2b

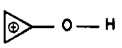

3a


3b


3c


4a


4b


4c

What is the preferred conformation of these dications? The hydroxycyclopropenium cation is more stable in the bent planar conformation **4a**, where the empty cationic $2p(C^+)$ orbital is conjugated with the $2p_y$ lone pair of oxygen. In the perpendicular conformation **4b**, the $2p(C^+)$ orbital is conjugated with the sp^2 lone pair of oxygen. Due to its lower energy[8] an sp^2 orbital is less effective than a 2p orbital in stabilizing an adjacent empty orbital.[9] Consequently, **4b** is less stable than **4a** by 11.3 kcal mol^{-1} (4-31G, Table I). In the dications the situation is more complex. In the bent planar conformations (e.g., **1a**) only *one* lone pair [i.e., $2p_y(O)$] is conjugated with the two electron deficient rings. In the bent perpendicular conformations (e.g., **1b**) on the other hand, each ring is conjugated with a different lone pair of oxygen so that two lone pairs participate in conjugation. Linear perpendicular conformations (e.g., **1d**) which have a pseudoallenic structure are especially attractive in this respect. Linearization at oxygen is, however, unfavorable energetically,[10] because the $sp^2(O)$ lone pair is transformed to a $2p(O)$ lone pair of higher energy.[8] Is the stabilization resulting from such double conjugation large enough to favor the perpendicular structures (e.g., **1b** or **1d**) over the planar structures (e.g., **1a**)? Qualitative arguments do not lead to a secure prediction.

The calculations point to a delicate balance between the various effects, resulting in a relatively small energy difference between the planar and the perpendicular conformations. The dicyclopropenylium ether dication is most stable in the *bent planar conformation* **1a** (arc ∠COC = 119.6°, STO-3G) but the rotation barrier around the COC bonds are remarkably small (Table I). The **1a**–**1b** energy difference is 5.85 kcal mol^{-1} (4-31G, 5.55 kcal mol^{-1} at STO-3G), much smaller than the corresponding rotation barriers in **4** (11.3 kcal mol^{-1}, 4-31G),[11a] $HOCH_2^+$ (22.5 kcal

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[1] Stang, P. J.; Maas, G.; Fisk, T. E. *J. Am. Chem. Soc.* **1980**, *102*, 6361. Stang, P. J.; Maas, G.; Smith, D. L.; McCloskey, J. A. *Ibid.*, in press.

[2] For recent reviews of MO calculations of carbenium ions, see: (a) Hehre, W. J. In "Applications of Electronic Structure Theory"; Schaefer, H. F., III. Ed.; Plenum Press: New York, **1977**; Vol. 4, pp 277–331. (b) Radom, L.; Poppinger, D.; Haddon, R. C. In "Carbonium Ions"; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, **1976**; Vol. 5, pp 2303–2426.

[3] For recent calculations of dications, see: (a) Clark, T.; Weiss, R. *J. Org. Chem.* **1980**, *45*, 1790. (b) Radom, L.; Schaefer, H. F., III. *J. Am. Chem. Soc.*, **1977**, *99*, 7522. (c) Craig, D. P.; Radom, L.; Schaefer, H. F., III *Aust. J. Chem.* **1978**, *31*, 261. (d) Borden, W. T.; Davidson, E. R.; Feller, D. *J. Am. Chem. Soc.* **1980**, *102*, 5302.

[4] Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285, 1294, 1302.

[5] The Gaussian 70 series of programs were used: Hehre, W. J.; Latham, W. A.; Ditchfield, R.; Newton, M.; Pople, J. A. Program No. 236, QCPE, Indiana University, Bloomington, IN.

[6] (a) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657. (b) Hehre, W. J., Pople, J. A. *Ibid* **1972**, *56*, 4233.

[7] The optimized structures of **1**–**4** are provided as supplementary material to this paper.

[8] In H_2O, for example, the energy difference between these orbitals is 2.1 eV. See: Turner, D. W. "Molecular Photoelectron Spectroscopy"; Wiley: London, 1970.

[9] Fleming, I. "Frontier Orbitals and Organic Chemical Reactions"; Wiley: London, 1976.

[10] Linear H_2O, for example, is by 35.6 kcal mol^{-1} (6-31G*) less stable than H_2O in its optimal geometry.

[11] (a) These rotation barriers are not sensitive to the basis set used; e.g., at 6-31G* the rotation barriers in **4** is 12.2 kcal mol^{-1}. (b) Bernardi, F.; Csizmadia, I. G.; Schlegel, H. B.; Wolfe, S. *Can. J. Chem.* **1975**, *53*, 1144. (c) Fărcasiu, D.; Horsley, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 4906.