

# Stereomutation of Methoxycarbenium Ions. 1. An Investigation of the Mechanism in Gaseous and Solution Phases

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**Abstract:** The stereomutation about the C–O partial double bond of hydroxy- and methoxy-substituted carbenium ions has been examined by using a combination of theoretical and experimental methods. Elaborate HF/6-31G\* and MP2/6-31G\* calculations on  $\text{CH}_2\text{OH}^+$  and  $\text{CH}_2\text{OCH}_3^+$  suggest that in the gaseous phase, the barriers to stereomutation by inversion are 22.9 and 17.5 kcal/mol, respectively, and by rotation are 25.9 and 26.3 kcal/mol, respectively. The stereomutation of  $\text{CH}_2\text{OCH}_3^+$  has also been examined experimentally in a series of  $\text{FSO}_3\text{H}/\text{SbF}_5$  solutions by using dynamic NMR methods. The measured barriers to stereomutation were found to be very dependent on the composition of the super acid medium used, ranging from 9.6 to 14.0 kcal/mol as the concentration of  $\text{SbF}_5$  was changed from a small to large molar excess. In view of the importance of solvent in determining the barriers for stereomutation of  $\text{CH}_2\text{OCH}_3^+$ , the effect of solvation on the theoretical barriers was investigated. The barrier to stereomutation by rotation was shown to be lowered by solvation while conversely the inversion barrier was raised. The magnitudes of these solvent effects are such that it is concluded that the lowest energy pathway to stereomutation of  $\text{CH}_2\text{OCH}_3^+$  in solution involves rotation. HF/6-31G\* calculations on a large number of substituted ions,  $\text{XCHOR}^+$ , show that the influence of the medium decreases rapidly if positive charge is delocalized by conjugative interactions of X with the carbenium center. In the case of substituted 1-hydroxy- and 1-methoxyallyl cations, stereomutation occurs exclusively by rotation due to a reduction of the  $\pi$  character of the CO bond in the ground state and conjugative stabilization of the rotational transition state. An analysis of the  $\pi$ -electron distribution shows that the rotational barrier can be predicted from the  $\pi$ -donor or  $\pi$ -acceptor ability of the substituent X.

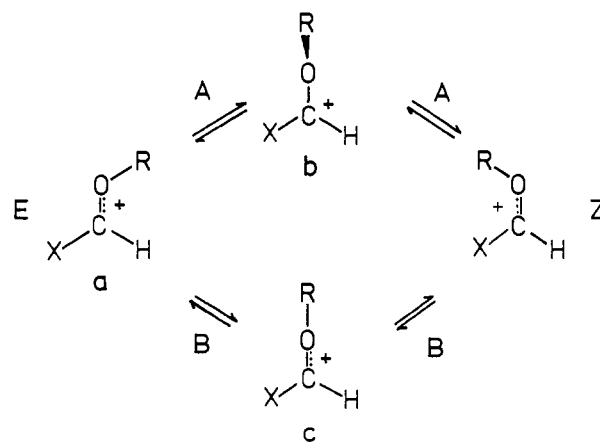
Theoretical investigations of carbenium ions are usually carried out under the assumption that characteristic properties such as structure, conformation, stability, and reactivity are similar in gaseous and solution phase. Although in most cases this assumption has proved to be a useful working hypothesis, it is also possible that solvent effects could lead to significant changes of molecular properties. For example, specific solvation at a carbenium carbon could lead to a charge being largely localized at this atom and a gain in energy. In the gaseous phase, however, delocalization of positive charge is energetically more favorable. Thus, free and solvated ions could possess different electronic structures which could result in different behaviors in gaseous and solution phase.

In this and the following paper in this issue, we describe our investigations into the influence of medium and substituents on the mechanism of stereomutation of hydroxy- and methoxy-substituted carbenium ions  $\text{XCHOR}^+$  ( $\text{R} = \text{H}, \text{CH}_3$ ). These ions exist in both the *E* and the *Z* conformations (Scheme I), with the two forms being separated by an appreciable energy barrier.<sup>2-5</sup>

Besides various intermolecular processes such as oxygen protonation or nucleophilic addition to the carbenium carbon, there are two intramolecular mechanisms which lead to an interconversion of *E* and *Z* conformations. These are rotation about the CO bond (path A, Scheme I) and inversion at the O atom (path B, Scheme I). While it is easy to formulate these two intramolecular mechanisms, it is much more difficult in practice to define which one is operative in a given system.

Model calculations on the stereomutation of protonated formaldehyde (1) and methoxycarbenium ion (2) give contradictory

Scheme I



results, with the more reliable ab initio investigations favoring the inversion path B.<sup>6-9</sup> Recently, Fărcașiu and Horsley<sup>8</sup> have calculated an inversion barrier of 12 kcal/mol for **2** which is seemingly in good accord with the experimentally determined stereomutation barrier ( $\Delta H^\ddagger = 11.9$  kcal/mol).<sup>4</sup> This led them to suggest that path B is the preferred mechanism for stereomutation.

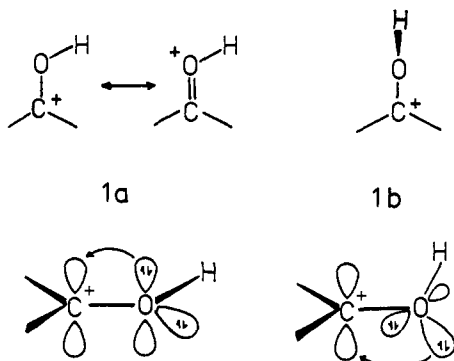
(6) Stereomutation barriers of  $\text{XCHOH}^+$  or  $\text{XCHOCH}_3^+$  have been calculated by: (a) Ros, P. *J. Chem. Phys.* **1968**, *49*, 4902-4916. (b) Purcell, K. F.; Collins, J. M. *J. Am. Chem. Soc.* **1970**, *92*, 465-469. (c) Bernardi, F.; Csizmadia, I. G.; Schlegel, H. B.; Wolfe, S. *Can. J. Chem.* **1975**, *53*, 1144-1153.

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 (2) (a) Olah, G. A.; White, A. M.; O'Brien, D. H. *Carbocation Ions 1968-1976* **1973**, *4*, 1697-1781. (b) Olah, G. A.; Bollinger, J. M. *J. Am. Chem. Soc.* **1967**, *89*, 2993.  
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 (4) Fărcașiu, D.; O'Donnell, J. J.; Wiberg, K. B.; Matturo, M. *J. Chem. Soc., Chem. Commun.* **1979**, 124-125.  
 (5) (a) Brouwer, D. M.; Mackor, E. L.; MacLean, C. *Recl. Trav. Chim. Pays-Bas* **1965**, *85*, 114-116. (b) Smart, B. E.; Reddy, G. S. *J. Am. Chem. Soc.* **1976**, *98*, 5593-5597. (c) Lustgarten, R. K.; Brookhart, M.; Winstein, S. *Tetrahedron Lett.* **1971**, 141-144. (d) Ramsey, B. G.; Taft, R. W. *J. Am. Chem. Soc.* **1966**, *88*, 3058-3063.

## Scheme II



There are both experimental and theoretical observations which make it advisable to reconsider this conclusion: (1) stereomutation barriers of 1-methoxyallyl cations have been reported to be close to 20 kcal/mol, and it is difficult to see why the barriers should be so much greater than those of **2**.<sup>3</sup> (2) Inversion barriers at a divalent O atom have been calculated to be rather high, ranging up to 40 kcal/mol.<sup>9</sup> (3) The 4-31G basis set used by Fărcașiu and Horsley is known to artificially favor structures with large COC angles.<sup>10</sup>

Prompted by these observations, we felt that a more detailed investigation of the stereomutation mechanism of carbenium ions XCHOR<sup>+</sup> was needed. In this and the following paper in this issue, we report the results of a two-pronged approach to the problem. A detailed examination of the stereomutation of hydroxy and methoxycarbenium ions has been undertaken by using ab initio calculations. This work has been extended to related substituted ions, and factors determining the stereomutation mechanisms have been explored. In the following paper in this issue, these results are extended to and coupled with detailed experimental work on some cinnamaldehyde-based systems.

## Method

All ab initio calculations on protonated aldehydes and methoxycarbenium ions have been carried out with the augmented split-valence 6-31G\* basis set.<sup>11</sup> Geometries of the parent compounds in their minimum energy (ME) (form a, Scheme I) and transition states (TS) for interconversion (forms b and c, Scheme I) have been obtained. To ensure that a reliable description of bond lengths and bond angles is obtained,<sup>12</sup> second-order Møller-Plesset (MP2) perturbation theory<sup>13</sup> has been used for the optimization of the structural parameters of **1** and **2**. MP2/6-31G\* geometries of the parent compounds have been maintained for Hartree-Fock (HF) calculations of substituted hydroxy- and methoxycarbenium ions 3-19. Standard bond lengths and angles<sup>14</sup> were used to determine the positions of the substituent atoms. For  $\alpha$ -substituted hydroxycarbenium ions such as protonated formic acid or protonated formamide, reoptimized structures have also been considered in order to make an assessment of the extent of interaction between the hydroxy group and substituent.

Barriers for rotation at the CO bond or inversion at the O atom have been determined at the HF level of theory. This level of theory was chosen since HF/6-31G\* values have been shown to be superior to MP2/6-31G\* values in related problems.<sup>15</sup>

## Results and Discussion

**Calculated Geometries.** The results of the MP2/6-31G\* optimization of **1** and **2** are shown in Figure 1. Comparison of the

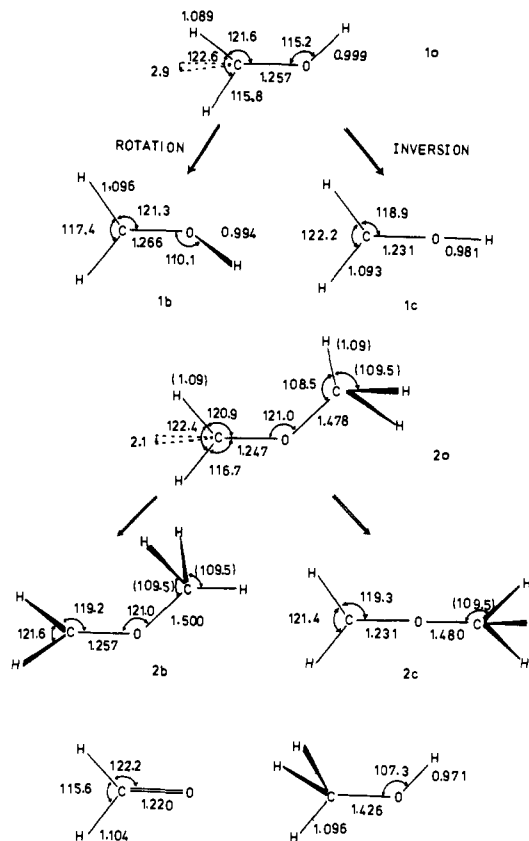


Figure 1. MP2/6-31G\* geometries of **1a**, **1b**, **1c**, **2a**, **2b**, **2c**, formaldehyde, and methanol. Assumed values are given in parentheses.

geometry of **1** with the theoretical geometries of formaldehyde and methanol obtained at the same level of theory reveals that protonation leads to only small distortions of the aldehyde geometry. The CO bond lengthens by 0.04 Å. The CH<sub>2</sub> group bends by 3° in the plane of the molecule to reduce H,H interactions. Correspondingly, the COH angle is considerably larger than the one of CH<sub>3</sub>OH, and the OH bond is longer by some 0.03 Å.

Rotation about the heavy atom bond of **1** by 90° causes a 0.01-Å increase of the CO bond length. This is a surprisingly small change in view of the valence bond description of **1a** and **1b** (see Scheme II), which suggests a significant increase of CO single bond character during rotation. However, partial delocalization of an O electron lone pair into the vacant 2p $\pi$ (C) orbital is possible both from the 2p $\pi$  (**1a**) and the sp<sup>2</sup> orbital (**1b**) of oxygen as shown in Scheme II. Electron donation from an sp<sup>2</sup> (O) orbital is less effective than from a p $\pi$ (O) orbital;<sup>7b</sup> however,  $\pi$  delocalization is also possible to some extent by donation from the p $\pi$ (O) orbital to the pseudo- $\pi^*$ -orbital of the CH<sub>2</sub> group. Thus, partial  $\pi$ -bond character of the CO bond is retained throughout rotation.

Inversion at the O atom leads to the unfavorable electronic configuration (sp)<sup>2</sup>(p<sub>x</sub>)<sup>2</sup>(p<sub>y</sub>)<sup>2</sup> for the oxygen atom with four electrons in high lying p $\pi$  orbitals. However, the energy of **1c** can be lowered by delocalization of p $\pi$ (O) electrons into the empty p $\pi$ (C<sup>+</sup>) orbital and the pseudo- $\pi^*$ -orbital of the CH<sub>2</sub> group. The calculated shortening of the CO bond during inversion can be rationalized in this way.

The geometric features of **2** are similar to those of **1**. The COC angle of **2a** is rather large (121°), probably because of enhanced H,H interactions. The most stable conformation of **2a** is equivalent to that found for propene, which has been explained in terms of bonding and antibonding secondary overlap between  $\pi$  and  $\pi^*$  MOs of the unsaturated heavy atom linkage and the CH<sub>3</sub> group.<sup>16</sup>

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(15) MP2 leads to a better description of delocalization effects most important for ME a. Thus, the description of both ME a and TS b becomes unbalanced which can only be corrected by going from MP2 to MP4. See, e.g.: Haddon, R. C.; Raghavachari, K. *J. Am. Chem. Soc.* **1983**, *105*, 118-120 or ref 18c.

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Table I. HF/6-31G\* and MP2/6-31G\* Energies<sup>a</sup>

ion	form a	form b	form c
A. XCHOY <sup>+</sup>			
(1) X = H, Y = H	-114.154 23	-114.112 92	-114.117 67
	-114.451 75	-114.401 52	-114.413 02
(2) X = H, Y = CH <sub>3</sub>	-153.200 50	-153.158 64	-153.172 61
	-153.630 50	-153.577 92	-153.597 48
(3) X = CH <sub>3</sub> , Y = H	-153.221 80	-153.179 99	-153.183 09
	-153.653 37	-153.602 95	-153.612 68
(4) X = NH <sub>2</sub> <sup>b</sup>	-169.248 39	-169.225 51	-169.211 05
(5) X = OH	-189.034 88	-189.006 55	-189.000 71
(6) X = F	-212.994 16	-212.963 51	-212.966 74
(7) X = NO <sub>2</sub>	-317.537 26	-317.497 90	-317.508 75
(8) X = F, Y = CH <sub>3</sub>	-252.042 51	-252.014 69	-252.025 51
B. XCH=CHCHOY <sup>+</sup>			
(9) X = H, Y = H	-191.081 98	-191.050 01	-191.042 91
(10) X = CH <sub>3</sub>	-230.132 13	-230.102 28	-230.092 35
(11) X = NH <sub>2</sub> <sup>b</sup>	-246.143 22	-246.119 08	-246.102 32
(11') X = NH <sub>2</sub> <sup>c</sup>	-246.119 01	-246.081 40	-246.072 48
(12) X = OH	-265.946 63	-265.918 55	-265.906 65
(13) X = F	-289.918 95	-289.887 62	-289.880 29
(14) X = CN	-282.788 37	-282.755 10	-282.750 16
(15) X = CHO	-303.790 92	-303.757 80	-303.751 99
(16) X = NO <sub>2</sub>	-394.494 39	-394.458 47	-394.457 02
(17) X = NF <sub>2</sub>	-443.625 45	-443.599 00	-443.585 74
(18) X = H, Y = CH <sub>3</sub>	-230.116 98	-230.083 42	-230.085 70
(19) X = F	-328.959 17	-328.926 95	-328.926 62

<sup>a</sup>Energies in hartree. The first entry gives the HF, the second the MP2 energy. <sup>b</sup>N atom is sp<sup>2</sup> hybridized. <sup>c</sup>N atom is sp<sup>3</sup> hybridized.

Table II. Stabilization Energies of Some Carbenium Ions Relative to CH<sub>3</sub><sup>+</sup><sup>a</sup>

ion <sup>+</sup> CH <sub>2</sub> X	HF/ STO-3G <sup>b</sup>	HF/ 6-31G*	MP2/ 6-31G*	exptl <sup>d</sup>
X = CH <sub>3</sub>	30.9	30.1 <sup>c</sup>	32.4 <sup>c</sup>	40.3
X = NH <sub>2</sub>	93.8	84.4	103.6	97.1 <sup>e</sup>
X = OH (1)	66.0	52.7	69.8	65.5
X = OCH <sub>3</sub> (2)		64.9	80.5	78

<sup>a</sup>The stabilization energy is defined as the energy of the formal reaction <sup>+</sup>CH<sub>2</sub>X + CH<sub>4</sub> → CH<sub>3</sub>X + CH<sub>3</sub><sup>+</sup>; all values in kilocalories/mole. <sup>b</sup>Reference 19. <sup>c</sup>Energies of carbenium ions from ref 18c. <sup>d</sup>ΔH<sub>f</sub><sup>o</sup> values of carbenium ions from ref 18a and b. <sup>e</sup>ΔH<sub>f</sub><sup>o</sup> values of neutral molecules from: Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1970. <sup>f</sup>Williams, D. H.; Bowen, R. D. *J. Am. Chem. Soc.* **1977**, *99*, 3192-3194.

The CO bond length is considerably larger than that of CH<sub>3</sub>OH or (CH<sub>3</sub>)<sub>2</sub>O.<sup>17</sup>

When **2a** is rotated into the perpendicular form **2b** and the structure optimized, the COC angle widens to 180°. That is, at the MP2/6-31G\* level of theory, no minimum energy path leading to a rotational TS can be found. Similar observations have been made at lower levels of theory.<sup>8</sup> The geometry shown for **2b** in Figure 1 has been obtained by keeping the COC angle at 121° (rigid rotor model).

**Energies.** Ab initio energies of **1-19** are summarized in Table I. In order to make an assessment of the reliability of the calculated molecular energies, theoretical and experimental energy differences are compared in Tables II and III. Table II contains stabilization energies of α-substituted carbenium ions measured relative to CH<sub>3</sub><sup>+</sup>.<sup>18,19</sup> MP2/6-31G\* stabilization energies are clearly in better accord with experimental data than HF/6-31G\*

(17) The experimental CO bond length of (CH<sub>3</sub>)<sub>2</sub>O is 1.410 Å. See: Gordy, W.; Cook, R. L. "Microwave Molecular Spectra"; Interscience; New York, 1970; p 701.

(18) Experimental ΔH<sub>f</sub><sup>o</sup> values of carbenium ions from (a) Loosing, F. P. *J. Am. Chem. Soc.* **1977**, *99*, 7526-7530. (b) Houle, F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 4067-4074. (c) Raghavachari, K.; Whiteside, R. A.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5649-5657.

(19) Apeloig, Y.; Schleyer, P. v. R.; Pople, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 1291-1296 and references cited therein.

Table III. Absolute and Relative Proton Affinities of Compounds **20-24**<sup>a</sup>

molecule XCHO	abs proton affinity			rel proton affinity		
	HF/ 6-31G*	MP2/ 6-31G*	exptl <sup>b</sup>	HF/ 6-31G*	MP2/ 6-31G*	exptl <sup>b</sup>
(20) X = H	180.7	173.7	174.6	0	0	0
(21) X = CH <sub>3</sub>	193.9	185.9	185.0	13.2	12.2	10.4
(22) X = NH <sub>2</sub>	202.4		194	21.7		19.4
(23) X = OH	186.0	182.6	180.1	5.3	8.9	5.5
(24) X = F	165.7	162.3		-15.0	-11.4	

<sup>a</sup>Relative PA values correspond to the energy of the proton-transfer reaction H<sub>2</sub>CO + XCHOH<sup>+</sup> → H<sub>2</sub>COH<sup>+</sup> + XCHO. All values in kilocalories/mole; for **22-24** STO-3G reoptimized geometries have been used (ref 7e). <sup>b</sup>Experimental values from ref 20.

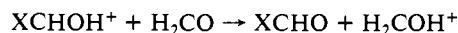
Table IV. Comparison of Theoretical Stereomutation Barriers<sup>a</sup>

molecule	rotation	inversion	method <sup>b</sup>	ref
<sup>+</sup> CH <sub>2</sub> ---OH (1)	25.9	22.9	HF/6-31G*	this work, 7i
<sup>+</sup> CH <sub>2</sub> ---OCH <sub>3</sub> (2)	26.3 <sup>c</sup>	17.5	HF/6-31G*	this work, 7i
CH <sub>2</sub> ---OO	32.1	40.7	MP2/6-31G*	9
<sup>+</sup> CH <sub>2</sub> ---CH---CH <sub>2</sub>	33.7		HF/6-31G**	18c
CH <sub>2</sub> =NH	58.1	27.8	HF/DZ	21
	64.5		CI/DZ+P	22
CH <sub>2</sub> =NCH <sub>3</sub>	58.0	23.8	HF/DZ	21
CH <sub>2</sub> =CH <sup>-</sup>		40.3	SCEP/DZ+s	23
HN=NH	71.0	51.9	HF/DZ	21
HN=NCH <sub>3</sub>		52.6; <sup>d</sup>	HF/DZ	21
		46.1 <sup>e</sup>		
CH <sub>2</sub> =NH <sub>2</sub> <sup>+</sup>	76.6		HF/DZ	21
CH <sub>2</sub> =NHCH <sub>3</sub> <sup>+</sup>	73.1		HF/DZ	21
HOH		37.2	MP2/6-31G*	this work, 9
CH <sub>3</sub> OH		32.5	HF/DZ	24

<sup>a</sup>All values in kilocalories/mole. <sup>b</sup>DZ: double-ζ basis; DZ+P: DZ basis plus polarization functions; DZ+s: DZ basis plus diffuse s functions. <sup>c</sup>Rigid rotation. <sup>d</sup>H inverts. <sup>e</sup>CH<sub>3</sub> inverts.

values. The high stabilization energy of **1** suggests that the OH group acts primarily as a π donor rather than a π acceptor. Replacement of the hydroxy group by a methoxy group leads to an increase of the π-donor ability of the O atom as is revealed by the data of Table II.

Table III contains proton affinities (PA) of formaldehyde (**20**), acetaldehyde (**21**), formamide (**22**), formic acid (**23**), and formyl fluoride (**24**). MP2/6-31G\* PA values coincide with experimental data<sup>20</sup> within 1 kcal/mol. This is far better than can be achieved at the HF level of theory. For example, HF/6-31G\* PAs are too large by 7-8 kcal/mol. On the other hand, relative PAs measured by the energy of the proton-transfer reaction



are well described at both the MP2 and HF level provided the 6-31G\* basis is employed.

Protonation of a carbonyl compound results in an electron transfer from the oxygen atom to the incoming proton. This is accompanied by a movement of electron density from carbon to the oxygen atom. The extent of this migration is critically dependent on the polarizability of the electron density, particularly the π density at the carbon atom. As the latter is enhanced by π-donor substituents, the stabilizing effect of an α substituent decreases in the order NH<sub>2</sub> > CH<sub>3</sub> > OH > F.

Since the data of Tables II and III were obtained by using different reference molecules, they provide no direct answer to the question whether the positive charge of **1a** is predominantly localized at C or O. A direct comparison of H<sub>2</sub>COCH<sub>3</sub><sup>+</sup> (**2**) and CH<sub>3</sub>CHOH<sup>+</sup> (**3**) reveals that **3** is more stable than **2** by 18

(20) (a) Yamdagni, R.; Kebarle, P. *J. Am. Chem. Soc.* **1976**, *98*, 1320-1324. (b) Wolf, J. F.; Staley, R. J.; Koppel, I.; Taagepera, M.; McIver, R. T., Jr.; Beauchamp, J. L.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 5417-5429. (c) Kebarle, P. *Annu. Rev. Phys. Chem.* **1977**, *28*, 445-476. For the PA value of NH<sub>2</sub>CHO see Note Added in Proof section of: (d) Brown, R. S.; Tse, A. *J. Am. Chem. Soc.* **1980**, *102*, 5222-5226.

**Table V.** Stereomutation of  $\text{CH}_2\text{OCH}_3^+$  in  $\text{FSO}_3\text{H}/\text{SbF}_5^a$ 

SbF <sub>5</sub> / precursor ratio	coalescence, temp. °C	rate const, s <sup>-1</sup>	temp, °C	$\Delta G^\ddagger$ , kcal/mol (mean)	$\Delta H^\ddagger$ , kcal/mol	$\Delta S^\ddagger$
3.7:1	~12	2 ± 1	-30	14.0 ± 0.2 <sup>b</sup>	11.7 ± 1	-7.0 ± 4
		4 ± 1	-21			
		15 ± 1	-11			
		28 ± 0.5	-1			
		57 ± 1	8			
3:1	~10	115 ± 5	17			
		12 ± 2	-20	13.7 ± 0.2		
		22 ± 3	-15			
		26 ± 2	-5			
		55 ± 2	0			
70 ± 3	5					
1.4:1	~-30	25 ± 2	-60	11.5 ± 0.5		
		40 ± 2	-40			
		130 ± 4	-30			
1.1:1	~-80	10 ± 8 <sup>c</sup>	-90	9.6 ± 1		
		70 ± 5 <sup>c</sup>	-80			
		150 ± 5	-70			

<sup>a</sup>Precursor used was  $\text{ClCH}_2\text{OCH}_3$ . <sup>b</sup>Calculated by using the Eyring equation. <sup>c</sup>Considerable viscosity broadening occurred giving rise to large errors.

kcal/mol<sup>18a</sup> (13.4, HF/6-31G\*; 14.4 MP2/6-31G\*). Thus, methyl substitution at C is clearly more stabilizing, suggesting that positive charge is preferentially located at the C atom.

**Stereomutation Barriers.** The calculated barriers to stereomutation of **1** and related systems are shown in Table IV. The rotational barrier for **1** is found to be 26 kcal/mol which is considerably lower than the barriers to rotation about C=C or C=N double bonds of related compounds.<sup>21-23</sup> The relatively low barrier suggests that the CO double bond character of **1a** is lower than that of the allyl cation (bond order 1.5), in as much as the barrier to rotation in the latter system is higher than that of **1a**. However, the lone pair interaction in the rotational TS **1b** has also to be considered.

The barriers to inversion of compounds  $\text{H}_2\text{CXH}$  decrease with increasing electronegativity of atom X, namely in the order C<sup>-</sup>, N, and O (Table IV). The energy of a  $2p\pi$  orbital of X decreases in this order, which means that the electron configuration  $2p_x^2 2p_y^2$  of the inversion TS becomes more favorable.

A  $\text{CH}_3$  group at the inverting heteroatom further stabilizes the TS by 4-5 kcal/mol (Table IV) with the largest effect being for inversion at an O atom. We attribute this effect to the possibility of  $p\pi(X)$  delocalization into the pseudo- $\pi^*$ -orbitals of the  $\text{CH}_3$  group. Also, the steric strain inherent in the ME of  $\text{CH}_2\text{XCH}_3^+$  is partially relieved in the inversion TS. In summary, the calculated configurational barriers compare favorably with those of related compounds.

**Preferred Stereomutation Mode of 1 and 2 in Gaseous and Solution Phases.** All previous ab initio calculations of the configurational barriers of **1** and **2**,<sup>6-9</sup> like those presented here, suggest that in each case the preferred stereomutation mode is inversion. Published theoretical values for the inversion barrier range from 12 to 25 kcal/mol while those for the rotational barrier vary between 25 and 35 kcal/mol.

Fărcașiu and Horsley<sup>4</sup> have examined experimentally the stereomutation of **2** in solution ( $\text{SO}_2\text{ClF}$ ) and reported an energy barrier ( $\Delta G^\ddagger$ ) of 12.9 kcal/mol. The value is in seemingly good agreement with the HF/4-31G inversion barrier calculated for **2** (12.1 kcal/mol). It was concluded on this basis that **1** and **2** stereomutate by inversion in both gaseous and solution phases.<sup>8</sup>

In view of the barrier values obtained with the 6-31G\* basis set, the HF/4-31G results are doubtful. For example, Fărcașiu,

Wiberg, et al. have obtained 4-31G stabilization energies of **1** and **2** which are 15-20 kcal/mol lower than experimental values (Table II). Obviously, the HF/4-31G approach severely underestimates the stabilities of **1a** and **2a**. The reason for this deficiency can easily be traced when comparing HF/4-31G<sup>8</sup> and MP2/6-31G\* geometries of **1a** and **2a**. In both cases the 4-31G basis overestimates the COC angle by 7-10°, an artifact arising from its tendency to exaggerate bond polarity and charge transfer in heteropolar bonds.<sup>10</sup> Thus, the linear TSs **1c** and **2c** are artificially stabilized with respect to **1a** and **2a**.

The HF/6-31G\* description does not suffer from these deficiencies. The computed values of 22.9 and 17.5 kcal/mol for inversion of **1** and **2**, respectively, are probably accurate within 1-2 kcal/mol.<sup>25</sup> This means that for **2** there is a significant discrepancy between theoretical and published experimental stereomutation barriers of 6-8 kcal/mol. Since such a discrepancy is unusual for conformational or configurational problems, we have looked for possible explanations.

**Reexamination of  $\text{CH}_2\text{OCH}_3^+$  Stereomutation.** The ion **2a** was generated by ionization of  $\text{ClCH}_2\text{OCH}_3$  in  $\text{FSO}_3\text{H}/\text{SbF}_5$ . The amount of chloroether was varied so as to give different molar ratios of  $\text{SbF}_5$  to  $\text{ClCH}_2\text{OCH}_3$  in the final solution. As the acidity of  $\text{FSO}_3\text{H}/\text{SbF}_5$  increases with the amount of  $\text{SbF}_5$  present, the smaller the ratio of  $\text{SbF}_5$  to  $\text{ClCH}_2\text{OCH}_3$  used, the lower the acidity of the resulting medium.

The low-temperature <sup>1</sup>H NMR spectra at 250 or 400 MHz of all the solutions were very similar with a singlet at  $\delta$  5.37 and doublets at  $\delta$  9.37 and 9.50,  $J = 20.8$  Hz. The spectra were essentially identical with those reported by Olah et al.<sup>2b</sup> and Fărcașiu et al.<sup>4</sup> and are consistent with the formation of  $\text{CH}_2\text{OCH}_3^+$ . As previously noted, the <sup>1</sup>H NMR spectra of each of the solutions exhibited reversible temperature dependence in which the low-field doublets merged into a singlet at higher temperatures. However, the coalescence temperatures observed were found to be very dependent on the composition of the acid medium used. The rates of exchange were determined in each case by line shape analyses. As can be seen from the data summarized in Table V, the free energy of activation for the stereomutation of **2a** systematically varies as the molar ratio of  $\text{SbF}_5$  to  $\text{ClCH}_2\text{OCH}_3$  is changed. There is more than a 4 kcal/mol difference in  $\Delta G^\ddagger$  between the most and least acidic media used in these experiments.

(21) Merenyi, G.; Wettermark, G.; Roos, B. *Chem. Phys.* **1973**, *1*, 340-347.

(22) Demuyck, J.; Fox, D. J.; Yamaguchi, Y.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1980**, *102*, 6204-6207.

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(25) The inversion barrier of  $\text{NH}_3$  calculated at the HF/6-31G\*//MP2/6-31G\* level of theory coincides with the experimental value within 0.6 kcal/mol.

In order to check whether the medium effect noted above is also occurring in  $\text{SbF}_5/\text{SO}_2\text{ClF}$ , the medium used by Fărcașiu and co-workers,<sup>4</sup> cation **2a** was prepared in this solvent. With a 6:1 molar ratio of  $\text{SbF}_5$  to  $\text{ClCH}_2\text{OCH}_3$  in  $\text{SO}_2\text{ClF}$ , we were unable to detect any line broadening of the  $\text{CH}_2$  resonances in the  $^1\text{H}$  NMR spectrum of **2a** at 10 °C. Clearly the coalescence temperature must be considerably above this temperature and much higher than 1 °C, as reported by Fărcașiu.<sup>4</sup> It would seem clear that there is a substantial medium effect occurring in  $\text{SO}_2\text{ClF}$ . The low boiling point of  $\text{SO}_2\text{ClF}$  makes a quantitative examination at higher temperatures very difficult, and a systematic study was not carried out.

While the highest barrier to stereomutation of **2** observed here is greater than that reported by Fărcașiu and is closer to the calculated barrier for the inversion process, the presence of such a large medium dependence clearly indicates that the involvement of medium cannot be neglected in this reaction. As the barrier for stereomutation is lowered in the less acidic, more nucleophilic media, it would seem that some degree of ion pairing, specific solvation, or nucleophilic capture is occurring at the transition state for the stereomutation. This means that before we reach a firm conclusion as to the mechanism of the stereomutation of **2**, the effect of solvation on the two processes has to be considered.

Although solvation energies (SE) of ions can be quite large, solvation effects on relative carbocation stabilities are normally small.<sup>26</sup> This changes, however, as soon as solvation of specific atoms rather than general solvation of the whole ion occurs. The importance of specific solvation increases with increasing charge localization as has been demonstrated by Arnett and Petro<sup>26a</sup> for the ionization of alkyl halides in superacid media.

A simple way to model the effects of solvation on the stereomutation barriers of **1** and **2** is achieved by considering a charge-transfer complex between **1** or **2** and an electron-donating solvent molecule (or solvated counterion). The relative magnitude of the stabilizing charge-transfer interactions can be estimated with the help of second-order perturbation theory where for reasons of simplicity only the HOMO-LUMO interaction is considered.<sup>27</sup> This leads to

$$SE = a \frac{\sum_i c_{iL}^2}{\epsilon_L - \epsilon_H} \quad (1)$$

where  $a$  is a proportionality constant;  $i$  denotes a component of the LUMO (L) of the carbenium ion,  $c_{iL}$  the coefficient of this component,  $\epsilon_L$  the LUMO energy of the carbenium ion, and  $\epsilon_H$  the HOMO energy of the solvent molecule.

Assuming an  $\epsilon_H$  of about 13 eV<sup>28</sup> and utilizing calculated HF/6-31G\* orbital energies ( $\epsilon_L(\mathbf{1a}) = -5.19$ ;  $\epsilon_L(\mathbf{1b}) = -6.23$ ;  $\epsilon_L(\mathbf{1c}) = -4.76$  eV) and coefficients, eq 1 suggests that the SE should increase with decreasing charge delocalization in the order  $\mathbf{c} < \mathbf{a} < \mathbf{b}$ . This means that the barrier to rotation will be reduced in solution while the barrier to inversion will be enhanced in solution.

The predictions of this simple model are confirmed by MINDO/3 stabilization energies,  $\Delta\Delta H_s$ , of  $\text{RCHOH}^+$  due to HCl complexation:

$$\Delta\Delta H_s = \Delta H_f^\circ(\text{RCHOH}^+) + \Delta H_f^\circ(\text{HCl}) - \Delta H_f^\circ(\text{HCl}\cdots\text{RCHOH}^+) \quad (2)$$

For **1**,  $\Delta\Delta H_s$  values are 11.0 (**1a**), 19.5 (**1b**), and 10.1 kcal/mol (**1c**), thus leading to a 8.5 kcal/mol decrease of the barrier to rotation and an 1 kcal/mol increase of the barrier to inversion.<sup>29</sup>

(26) (a) Arnett, E. M.; Petro, C. *J. Am. Chem. Soc.* **1978**, *100*, 5402-5407, 5408-5416. (b) Taft, R. W.; Wolf, J. F.; Beauchamp, J. L.; Scorrano, G.; Arnett, E. M. *J. Am. Chem. Soc.* **1978**, *100*, 1240-1249.

(27) (a) Dewar, M. J. S.; Dougherty, R. C. "The PMO Theory of Organic Chemistry"; Plenum Press: New York, 1975. (b) Jorgensen, W. L. *J. Am. Chem. Soc.* **1977**, *99*, 280-283.

(28) The first vertical ionization potential of  $\text{SO}_2\text{F}_2$  is 13.7 eV and the one of  $\text{SO}_2\text{Cl}_2$  12.4 eV. Solouki, B.; Bock, H.; Appel, R. *Chem. Ber.* **1975**, *108*, 897-913.

Table VI. HF/6-31G\* Stabilization Energies of Carbenium Ions  $\text{XCHOH}^+$  and  $\text{XCH}=\text{CHCHOH}^+$ <sup>a</sup>

ion	stabilization energy		
	form a	form b	form c
A. $\text{XCHOH}^+$			
(3) X = CH <sub>3</sub>	20.9	20.6	19.6
(4) X = NH <sub>2</sub>	47.6	59.2	47.1
(5) X = OH	21.3	29.3	19.8
(6) X = F	-5.3	1.3	0.4
(7) X = NO <sub>2</sub>	-48.3	-47.7	-43.3
(9) X = CH=CH <sub>2</sub>	32.9	38.6	31.3
B. $\text{XCH}=\text{CHCHOH}^+$			
(10) X = CH <sub>3</sub>	7.4	8.8	6.9
(11) X = NH <sub>2</sub>	23.5	28.4	22.3
(12) X = OH	7.3	9.8	6.7
(13) X = F	-6.7	-6.2	-6.5
(14) X = CN	-17.8	-18.6	-17.3
(15) X = CHO	-12.0	-12.7	-11.9
(16) X = NO <sub>2</sub>	-28.8	-30.2	-27.8
(17) X = NF <sub>2</sub>	7.1	10.6	6.7

<sup>a</sup>  $\text{XCHOH}^+$  stabilization energies are given relative to  $\text{CH}_2\text{OH}^+$  according to  $\text{XCHOH}^+ + \text{CH}_3\text{CH}_3 \rightarrow \text{XCH}_2\text{CH}_3 + \text{CH}_2\text{OH}^+$ .  $\text{XCH}=\text{CHOH}$  stabilization energies are given relative to  $\text{CH}_2=\text{CHCHOH}^+$  according to  $\text{XCH}=\text{CHCHOH}^+ + \text{CH}_2\text{CH}_2 \rightarrow \text{XCHCH}_2 + \text{CH}_2=\text{CHCHOH}^+$ . All values in kilocalories/mole. Forms a, b, and c correspond to ME, rotational and inversional TS.

Table VII. Theoretical and Experimental Stereomutation Barriers of Ions  $\text{XCHOH}^+$  and  $\text{XCH}=\text{CHCHOH}^+$ <sup>a</sup>

ion	HF/6-31G*			population analysis <sup>g</sup>	
	rotation	inversion	exptl	$P_x(\text{CO})$	$P_x(\text{CX})$
A. $\text{XCHOY}^+$					
(1) X = H, Y = H	25.8	22.9		0.282	0
(2) X = H, Y = CH <sub>3</sub>	26.3	17.5	14.7 <sup>b</sup>	0.313	0
(3) X = CH <sub>3</sub> , Y = H	26.2	24.2		0.264	0.047
(4) X = NH <sub>2</sub>	14.3	23.4		0.171	0.252
(5) X = OH	17.8	21.4		0.214	0.156
(6) X = F	19.2	17.2		0.245	0.096
(7) X = NO <sub>2</sub>	25.2	17.9		0.282	0.046
(8) X = F, Y = CH <sub>3</sub>	17.5	10.7		0.277	0.088
B. $\text{XCH}=\text{CHCHOY}^+$					
(9) X = H, Y = H	20.1	24.5		0.206	0.170
(10) X = CH <sub>3</sub>	18.7	25.0	18.5 <sup>c</sup>	0.192	0.192
(11) X = NH <sub>2</sub> <sup>e</sup>	15.2	25.7		0.150	0.257
(11') X = NH <sub>2</sub> <sup>f</sup>	19.1	24.7		0.195	0.186
(12) X = OH	17.6	25.1		0.178	0.219
(13) X = F	19.6	24.3		0.200	0.185
(14) X = CN	20.9	24.0		0.212	0.161
(15) X = CHO	20.8	24.4		0.212	0.162
(16) X = NO <sub>2</sub>	22.5	23.5		0.228	0.137
(17) X = NF <sub>2</sub>	16.6	24.9		0.168	0.234
(18) X = H, Y = CH <sub>3</sub>	21.1	19.6	19.9 <sup>d</sup>	0.237	0.154
(19) X = F	20.2	23.6		0.230	0.167

<sup>a</sup> All energy values in kilocalories/mole. <sup>b</sup> This work. <sup>c</sup> Barrier of  $\text{CH}_3\text{CHCHCHOCH}_3^+$ , ref 3. <sup>d</sup> Reference 3. <sup>e</sup> N atom is  $\text{sp}^2$  hybridized. <sup>f</sup> N atom is  $\text{sp}^3$  hybridized. <sup>g</sup>  $P_x$  values are given for form a.

According to both eq 1 and 2, solvation effects are considerably larger for form **b** of **1** and **2** than for the other forms. For larger carbenium ions such as **9** or **18**, solvation effects become considerably smaller and similar in magnitude, however, solvation effects will always act in the way that inversion barriers are slightly increased while rotation barriers are decreased.

In order to make a more quantitative assessment of the expected influence of the solvent on the stereomutation barrier, we have compared **2** with the  $\pi$ -isoelectronic allyl cation. Theoretical

(29) MINDO/3 (similar as MNDO) calculations of form **b** lead to an unrealistic large COH angle close to 180°. Therefore, this angle has been kept at the ab initio value (110°). Then, barrier values of 22 (rotation) and 8.3 kcal/mol (inversion) are obtained. The computed C,Cl distances are 2.144 (**1a**), 2.023 (**1b**), and 2.173 Å (**1c**).  $\Delta\Delta H_s$  values have been improved by CI calculations considering double excitations.

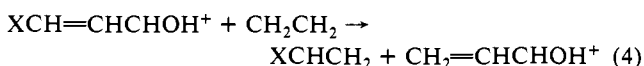
calculations suggest that the latter possesses a rotational barrier of 34 kcal/mol in the gaseous phase.<sup>18c</sup> In solution phase (SbF<sub>5</sub>/SO<sub>2</sub>ClF), however, the rotational barrier has been estimated to be 10 kcal/mol smaller due to specific solvation at the positive C atom.<sup>30</sup> A similar change of the SE during stereomutation of **1** or **2** would reduce the rotational barrier to about 16 kcal/mol which is not too far removed from the observed value considering the approximations made in this estimate. It should be noted however that at the same time, the inversion barrier would increase to a value above 20 kcal/mol. We conclude that **1** and **2** stereomutate by inversion (TS c) in the gaseous phase but by rotation (TS b) in solution phase.<sup>31</sup>

**Substituent Effects.** The influence of a substituent X on the stability of the carbenium ion XCHOH<sup>+</sup> can be determined by the energy of the formal reaction shown in eq 3. Results are summarized in Tables VI and VII.

As noted above,  $\pi$ - and/or  $\sigma$ -donor substituents positioned at the positively charged C atom stabilize **1** while the reverse is true in the case of  $\pi/\sigma$ -acceptor substituents. In order to distinguish



between  $\pi$  and  $\sigma$  effects, the protonated acroleins **10**–**17** have been investigated and their stabilization energies have been calculated by using eq 4. With these acrolein-based systems, possible  $\sigma$

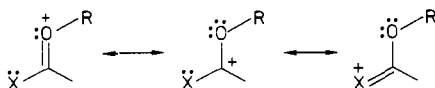


effects of the group X are largely absorbed by the unsaturated linkage, CH=CH, which separates X and the carbenium carbon atom. Thus, mainly  $\pi$  effects are measured by the reaction energy of eq 4.

HF/6-31G\* stabilization energies obtained in this way for the two types of system are summarized in Table VI. As can be seen the values confirm the increase (decrease) of stability of both systems due to a  $\pi$ -donor (acceptor) substituent X. They show also the expected decrease of substituent effects if X is no longer positioned at the positively charged C atom (compounds **10**–**17**).

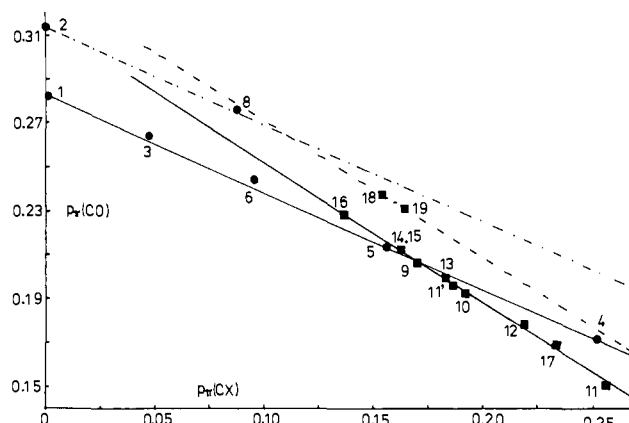
There is a significant increase in the stabilizing influence of a potential  $\pi$ -donor X in the rotational TS (forms b) which possess a more positively charged C atom than the ME (form a). In contrast, apart from **6** and **7**, the stabilization energies for the ME and inversion TS (forms a and c, respectively) are very similar, and no major effect of substituents on the barrier to inversion is observed. In the cases of **6** and **7**, extra stabilization seems to result from a depopulation of the high-lying  $p\pi$  (O) orbitals caused by the electron-withdrawing ability of the substituents. Apart from the two exceptions, values of the inversion barriers of substituted ions in the series **1**–**19** are in the range of 21.5–25 kcal/mol.

While the barriers to inversion in these ions do not depend on the substituents on the  $\alpha$  carbon, the rotational barriers (Table VII) show a large dependence and vary from 15 to 27 kcal/mol. This variation can be quantitatively described by considering the  $\pi$ -donor capacity of the substituent X. The height of the rotational

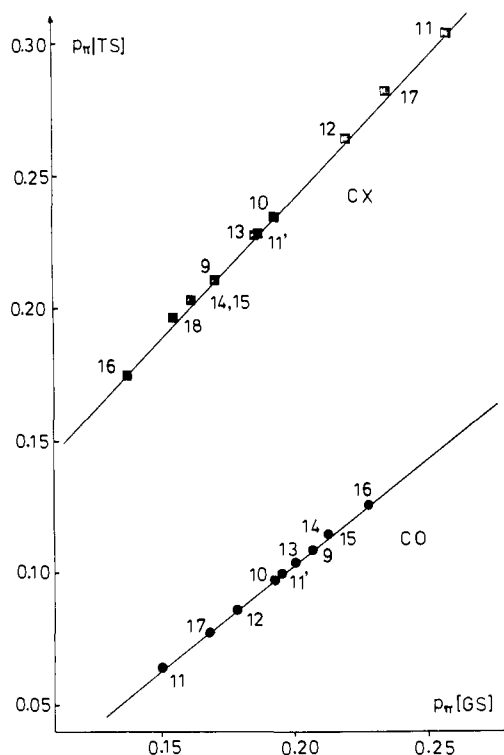


barrier will depend on the double bond character of the CO bond in form a, the minimum energy configuration, and the stabilization of the rotational TS b, which are both affected by the  $\pi$  contributions to the bond CX.

In Figure 2 we have plotted overlap populations  $p\pi(\text{CO})$  vs.  $p\pi(\text{CX})$  given in Table VII. For derivatives of both **1** and **9** there is a correlation between these two theoretical bond parameters: the CO  $\pi$ -bond character is inversely proportional to the CX



**Figure 2.** Relationship between HF/6-31G\*  $\pi$ -overlap populations of CX and CO bonds ( $\bullet$ ) protonated formaldehydes, ( $\blacksquare$ ) protonated acroleins). Assumed relationships for methoxycarbenium ions are indicated by dashed lines. (For numbering, see Table VI).



**Figure 3.** Relationship between ME and TS b  $\pi$ -overlap populations of CX and CO bonds. (For numbering, see Table VI).

$\pi$ -bond character; i.e., the higher the  $\pi$ -donor effect of X, the lower is the CO  $\pi$ -bond character. Although our data are limited, we expect that consideration of derivatives of the methoxycarbenium ions **2** and **18** will lead to lines parallel to the hydroxycarbenium ion correlations but shifted to larger  $p\pi(\text{CO})$  values.

When going from the ME a to the rotational TS b, the  $\pi$ -overlap populations of the CX bond increase by about 25% while those of the CO bond decrease by about 50%. There is a linear dependence of the  $\pi$ -bond character in TS b and the ME a (Figure 3), which indicates that the higher the  $\pi$ -donor capacity of X, the higher is the increase of  $p\pi(\text{CX})$  in TS b and the lower is the CO double bond character in both a and b.

Since the  $\pi$ -donor ability of X affects electron delocalization in both the ME and the rotational TS of ions XCHOR<sup>+</sup> in a consistent manner, as revealed by Figures 2 and 3, it is tempting to predict rotational barriers from either  $p\pi(\text{CX})$  or  $p\pi(\text{CO})$  values of ME forms a. This is done in Figure 4. In the case of protonated acroleins **9**–**17**, a linear correlation exists between barriers to rotation,  $\Delta E_R$ , and  $p\pi(\text{CO})$  overlap populations which can be

(30) Mayr, H.; Forner, W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1979**, *101*, 6032–6040.

(31) Competing proton-exchange processes with solvent can occur with **1** which will make observation of the intramolecular stereomutation difficult.

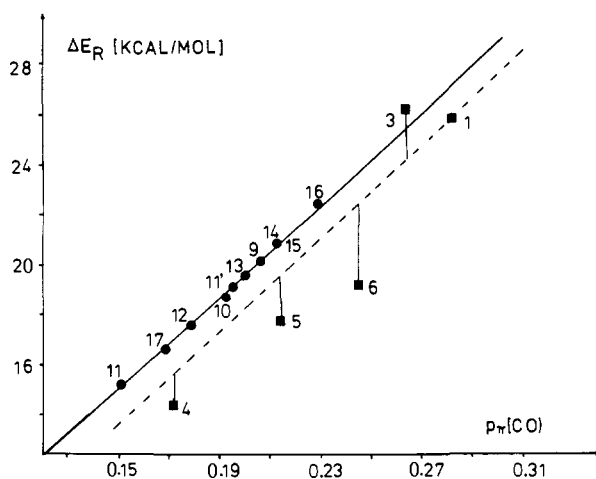
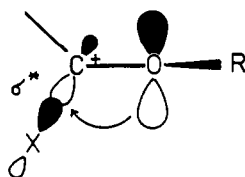


Figure 4. Dependence of calculated rotational barriers,  $\Delta E_R$ , on  $\pi$ -bond character of the CO bond in ME a. Assumed relationship for protonated formaldehydes is indicated by the dashed line. Deviations are given by vertical lines. (For numbering, see Table VI).

## Scheme III



extended to  $p\pi(CX)$  values because of the dependencies shown in Figure 2 and 3. Knowing the  $\pi$ -donor ability of X from relevant experimental or theoretical observations, the rotational barriers of derivatives of **9** or **18** can be predicted.

If only  $\pi$  effects were operative in  $\alpha$ -substituted carbenium ions **3**–**7**, a linear relationship between  $\Delta E_R$  and  $p\pi(CO)$  should also result for these ions. One can expect a line parallel to that of ions **9**–**17** and passing through the point for X = H, i.e., compound **1** (Figure 4). However, the actual barriers for X = NH<sub>2</sub>, OH, and F are lower by 1.3, 1.9, and 3.3 kcal/mol (Figure 4). Withdrawal of  $\sigma$  electrons would destabilize both form a and b, probably more so in the latter case due to the higher positive charge at the C atom. Accordingly, the rotational barrier should increase. The decrease of  $\Delta E_R$  suggested by the model approach inherent to Figure 4 indicates that another effect is operative. We note that the energy of the antibonding  $\sigma^*(CX)$  orbitals increases in the order  $\sigma^*(CF) < \sigma^*(CO) < \sigma^*(CN) < \sigma^*(CC)$ . Hence a stabilizing charge transfer from the  $2p\pi(O)$  orbital into the coplanar  $\sigma^*(CX)$  orbital becomes less effective when going from X = F to X = NH<sub>2</sub>. We conclude that  $\alpha$  substituents influence the rotational barriers by altering the  $\pi$ -bond character of the CO bond of the ME, form a, and by stabilizing the rotational TS via  $p\pi(O)$ – $\sigma^*(CX)$  interactions (Scheme III).

The same trends should be observed in the case of the methoxycarbenium ions. Rotational barriers will be shifted on the whole to somewhat larger barriers (1–2 kcal/mol for compound **9**–**17**), while a 4–5 kcal/mol decrease for the inversion barriers can be expected (Table VII) as compared with the hydroxycarbenium ion analogues.

**In conclusion**, the results given in Table VII suggest that the majority of protonated aldehydes stereomutate in the gaseous phase by inversion (ions **1**–**3**, **6**–**8**).<sup>31</sup> The mechanism of stereomutation changes to rotation if localization of positive charge at the carbenium carbon atom in the rotational TS b is facilitated either by substituents on this carbon or by solvation. The former effect prevails if the substituent X in XCHOR<sup>+</sup> is a relatively strong  $\pi$  donor as in the case of **4**, **5**, and the protonated acroleins **9**–**17**. As a result of the substantial charge delocalization in these cases, solvation should not significantly change the relative stabilities of the ME and rotational TS. This means that stereomutation barriers should be similar in the gaseous and solution phases. This should be the case, for example, for ClCHOCH<sub>3</sub><sup>+</sup> where the experimental barrier to stereomutation is greater than 17.3 kcal/mol (FSO<sub>3</sub>H/SbF<sub>5</sub>).<sup>32</sup> In solution, for those cations where delocalization of positive charge is not possible in the rotational TS (ions **1**–**3**), specific solvation at the positive C atom should take place, stabilizing the rotational TS. Hence, ions such as **1**–**3** should stereomutate in solution by rotation rather than inversion.

Changes of the stereomutation mechanism due to either solvent or substituent effects can be directly related to the polarizability of the  $\pi$ -electron distribution in cations XCHOR<sup>+</sup>. In **1** and **2** charge is pulled from the OR group (R = H, CH<sub>3</sub>) toward the positive C atom, thus leading to the relatively high rotational barriers. A nucleophilic solvent molecule or a  $\pi$ -donor substituent at C<sup>+</sup> displaces the  $\pi$  cloud to the O atom either by inter- or intramolecular stabilization of the positive charge. In this way, the  $\pi$  character of the CO bond is reduced and rotation is facilitated.

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**Registry No.** **1**, 17691-31-5; **2**, 23653-97-6; **3**, 17104-36-8; **4**, 50785-80-3; **5**, 16961-31-2; **6**, 61134-50-7; **7**, 95120-93-7; **8**, 29874-61-1; **9**, 57344-16-8; **10**, 71298-10-7; **11**, 69199-01-5; **12**, 95120-94-8; **13**, 95120-95-9; **14**, 95120-96-0; **15**, 95120-97-1; **16**, 95120-98-2; **17**, 95120-99-3; **18**, 69858-66-8; **19**, 95121-00-9; **20**, 50-00-0; **21**, 75-07-0; **22**, 75-12-7; **23**, 64-18-6; **24**, 1493-02-3; H<sub>2</sub>O, 7732-18-5; CH<sub>3</sub>CH<sub>2</sub><sup>+</sup>, 14936-94-8; CH<sub>2</sub>=NH·H<sup>+</sup>, 28963-72-6.

(32) ClCHOCH<sub>3</sub><sup>+</sup>, generated in FSO<sub>3</sub>H/SbF<sub>5</sub><sup>2</sup>, shows no averaging of the methyl signals of the two isomers in the <sup>1</sup>H NMR spectrum at +50 °C, the temperature at which the cations decompose.