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

Dieter Cremer, Jürgen Gauss, Ronald F. Childs, and Christopher Blackburn

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 CH2OH+ and CH2OCH3+ 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 CH3CHOH+ has also been examined experimentally in a series of FS03H/SbF5 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 SbF5 was changed from a small to large molar excess. In view of the importance of solvent in determining the barriers for stereomutation of CH3CHOH+, 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 CH3CHOH+ in solution involves rotation. HF/6-31G* calculations on a large number of substituted ions XCHOR+, show that the influence of the medium decreases rapidly if positive charge is delocalized by conjugative interactions with the carbenium center. In the case of substituted 1-hydroxy- and 1-methoxy-carbenium ions, stereomutation occurs exclusively by rotation due to a reduction of the π-character of the CO bond in the ground state and conjugative stabilization of the rotational transition state. An analysis of the π-electron distribution shows that the rotational barrier can be predicted from the π-donor or π-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 XCHOR+ (R = H, CH3). These ions exist in both the E and the Z conformations (Scheme I), with the two forms being separated by an appreciable energy barrier.2–5 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 methoxy-carbenium ion (2) give contradictory results, with the more reliable ab initio investigations favoring the inversion path B.6–8 Recently, Farcășiu and Horsley8 have calculated an inversion barrier of 12 kcal/mol for 2 which is seemingly in good accord with the experimentally determined stereomutation barrier (∆H° = 11.9 kcal/mol).4 This led them to suggest that path B is the preferred mechanism for stereomutation.


There are both experimental and theoretical observations which make it advisable to reconsider this conclusion: (1) stereomutation barriers of 1-methoxycarboxylic acid 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. (2) Inversion barriers at a divalent O atom have been calculated to be rather high, ranging up to 40 kcal/mol. (3) The 4-31G basis set used by Fircagiu and Horsley is known to artificially favor structures with large COC angles.

Prompted by these observations, we felt that a more detailed investigation of the stereomutation mechanism of carbenium ions XCHOR⁺ 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 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. 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, second-order Möller-Plesset perturbation theory 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 methoxy-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.

**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 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 CH₃ group bends by 3° in the plane of the molecule to reduce H₃C interactions. Correspondingly, the COH angle is considerably larger than the one of CH₂OH, and the OH bond is longer by some 0.03 Å.

Rotation about the heavy atom bond of 2 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 2π(CO) orbital is possible both from the 2π(CO) and the sp² orbital (1b) of oxygen as shown in Scheme II. Electron donation from an sp² (O) orbital is less effective than from a π*(O) orbital; however, π delocalization is also possible to some extent by donation from the π*(O) orbital to the pseudo-π*-orbital of the CH₃ group. Thus, partial π-bound character of the CO bond is retained throughout rotation.

Inversion at the O atom leads to the unfavorable electronic configuration (sp²(π)³p(π))² for the oxygen atom with four electrons in high lying π orbitals. However, the energy of 1c can be lowered by delocalization of π*(O) electrons into the empty π*(C¹) orbital and the pseudo-π*-orbital of the CH₃ 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 H₃C 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 π and π* MOs of the unsaturated heavy atom linkage and the CH₃ group.

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

<table>
<thead>
<tr>
<th>ion</th>
<th>form a</th>
<th>form b</th>
<th>form c</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) X = H, Y = H</td>
<td>-114.1523</td>
<td>-114.11292</td>
<td>-114.1176</td>
</tr>
<tr>
<td>(2) X = H, Y = CH₃</td>
<td>-114.45175</td>
<td>-114.40152</td>
<td>-114.4102</td>
</tr>
<tr>
<td>(3) X = CH₃, Y = H</td>
<td>-153.60000</td>
<td>-153.15864</td>
<td>-153.17261</td>
</tr>
<tr>
<td>(4) X = NH₃</td>
<td>-153.63573</td>
<td>-153.57792</td>
<td>-153.59748</td>
</tr>
<tr>
<td>(5) X = OH</td>
<td>-153.23110</td>
<td>-153.17999</td>
<td>-153.18309</td>
</tr>
<tr>
<td>(6) X = F</td>
<td>-192.99416</td>
<td>-212.96351</td>
<td>-212.9662</td>
</tr>
<tr>
<td>(7) X = NO₂</td>
<td>-213.57726</td>
<td>-213.49790</td>
<td>-213.50875</td>
</tr>
<tr>
<td>(8) X, F, Y = CH₃</td>
<td>-252.04251</td>
<td>-252.01469</td>
<td>-252.05251</td>
</tr>
</tbody>
</table>

*Energies in hartree. The first entry gives the HF, the second the MP2 energy. *N atom is sp³ hybridized. *N atom is sp³ hybridized.

**Table II.** Stabilization Energies of Some Carbocation Relative to CH₃⁺

<table>
<thead>
<tr>
<th>ion</th>
<th>CH₂X</th>
<th>HF/STO-3G</th>
<th>MP2/6-31G*</th>
<th>MP2/6-31G*</th>
<th>exptl</th>
</tr>
</thead>
<tbody>
<tr>
<td>X = CH₃</td>
<td>30.9</td>
<td>30.1</td>
<td>32.4</td>
<td>40.3</td>
<td></td>
</tr>
<tr>
<td>X = NH₃</td>
<td>93.8</td>
<td>94.4</td>
<td>103.6</td>
<td>97.1</td>
<td></td>
</tr>
<tr>
<td>X = OH</td>
<td>66.0</td>
<td>52.7</td>
<td>69.8</td>
<td>65.5</td>
<td></td>
</tr>
<tr>
<td>X = OCH₃</td>
<td>64.9</td>
<td>80.5</td>
<td>78.5</td>
<td>78.5</td>
<td></td>
</tr>
</tbody>
</table>


The CO bond length is considerably larger than that of CH₃OH or (CH₃)₂O. 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. 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 carbocation ions measured relative to CH₃⁺. MP2/6-31G* stabilization energies are clearly in better accord with experimental data than HF/6-31G*.

**Table III.** Absolute and Relative Proton Affinities of Compounds 20–24

<table>
<thead>
<tr>
<th>molecule</th>
<th>rotat-</th>
<th>inversion</th>
<th>method</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃OH⁺</td>
<td>72.9</td>
<td>22.9</td>
<td>HF/6-31G*</td>
<td>this work</td>
</tr>
<tr>
<td>CH₃OH⁺</td>
<td>72.3</td>
<td>17.5</td>
<td>HF/6-31G*</td>
<td>this work</td>
</tr>
<tr>
<td>CH₃OH⁺</td>
<td>32.1</td>
<td>40.7</td>
<td>MP2/6-31G*</td>
<td>9</td>
</tr>
<tr>
<td>CH₃CHO⁺</td>
<td>33.7</td>
<td>27.8</td>
<td>HF/6-31G*</td>
<td>18c</td>
</tr>
<tr>
<td>CH₃NH⁺</td>
<td>58.1</td>
<td>50.9</td>
<td>HF/6-31G*</td>
<td>21</td>
</tr>
<tr>
<td>CH₃CH₂NH⁺</td>
<td>58.0</td>
<td>23.8</td>
<td>HF/6-31G*</td>
<td>22</td>
</tr>
<tr>
<td>CH₃CH₂NH⁺</td>
<td>40.3</td>
<td>40.3</td>
<td>SCF/DZ+</td>
<td>23</td>
</tr>
<tr>
<td>CH₃CH₂NH⁺</td>
<td>74.0</td>
<td>51.9</td>
<td>HF/6-31G*</td>
<td>21</td>
</tr>
<tr>
<td>CH₃CH₂NH⁺</td>
<td>52.6</td>
<td>52.6</td>
<td>HF/6-31G*</td>
<td>24</td>
</tr>
</tbody>
</table>


values. The high stabilization energy of I 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), acetaldheyde (21), formamide (22), formic acid (23), and formyl fluoride (24). MP2/6-31G* PA values coincide with experimental data 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

XCHOH⁺ + H₂CO → XCHO + H₂COH⁺

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 NH₂ > CH₃ > 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 H₂COCH₂⁺ (2) and CH₃CH₂OH⁺ (3) reveals that 3 is more stable than 2 by 18
kcal/mol (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 considerandsally lower than the barriers to rotation about C=C or C=N double bonds of related compounds. 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 H2CXH decrease with increasing electronegativity of atom X, namely in the order C-, N, and O (Table IV). The energy of a 2p or orbital of X decreases in this order, which means that the electron configuration 2p^3 of 2p^2 of the inversion TS becomes more favorable.

A CH3 group at the inverting heteroatom further stabilizes the TS by 4-5 kcal/mol (Table IV) with the largest effect being for the 4-31G basis. 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 were 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.

Fărașanu and Horsley have examined experimentally the stereomutation of 2 in solution (SO2ClF) and reported an energy barrier (ΔG*) 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 stereomute by inversion in both gaseous and solution phases.

In view of the barrier values obtained with the 6-31G* basis set, the HF/4-31G results are doubtful. For example, Fărașanu, 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 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. 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. 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 CH3OCH3** Stereomutation. The ion 2a was generated by ionization of CH3OCH3 in FSO2H/SbF5. The amount of chloroether was varied so as to give different molar ratios of SbF5 to CH3OCH3 in the final solution. As the acidity of FSO2H/SbF5 increases with the amount of SbF5 present, the smaller the ratio of SbF5 to CH3OCH3 used, the lower the acidity of the resulting medium.

The low-temperature °H NMR spectra at 250 or 400 MHz of all the solutions were very similar with a singlet at δ 5.37 and doublets at δ 9.37 and 9.50, J = 20.8 Hz. The spectra were essentially identical with those reported by Obita et al. and Fărașanu et al. and are consistent with the formation of CH3OCH3. As previously noted, the °H NMR spectra of each of the solutions exhibited irreversible 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 SbF5 to CH3OCH3 is changed. There is more than a 4 kcal/mol difference in ΔG* between the most and least acidic media used in these experiments.

**Table V. Stereomutation of CH3OCH3 in FSO2H/SbF5.**

<table>
<thead>
<tr>
<th>SbF5/prc ratio</th>
<th>coalescence, temp. °C</th>
<th>rate const, s^-1</th>
<th>temp. °C</th>
<th>ΔG°*, kcal/mol (mean)</th>
<th>ΔH°*, kcal/mol</th>
<th>ΔS°</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.7:1</td>
<td>~12</td>
<td>2 ± 1</td>
<td>30</td>
<td>14.0 ± 0.2*</td>
<td>11.7 ± 1</td>
<td>-7.0 ± 4</td>
</tr>
<tr>
<td>3:1</td>
<td>~10</td>
<td>12 ± 2</td>
<td>-20</td>
<td>13.7 ± 0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.4:1</td>
<td>~30</td>
<td>25 ± 2</td>
<td>-60</td>
<td>11.5 ± 0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1:1:1</td>
<td>~80</td>
<td>10 ± 8'</td>
<td>-90</td>
<td>9.6 ± 1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Precursor used was CICH2OCH3. Calculated by using the Eyring equation. Considerable viscosity broadening occurring give rise to large errors.

(25) The inversion barrier of NH3 calculated at the HF/6-31G*/MP2/6-31G* level of theory coincides with the experimental value within 0.6 kcal/mol.
Stereoemutation of Methoxycarbenium Ions.

In order to check whether the medium effect noted above is also occurring in SF_2Cl/So_2ClF, the medium used by Farcas and co-workers,\(^\text{c}\) form 2a was prepared in this solvent. With a 6:1 molar ratio of SF_2Cl to CICH_2OCH_3 in SO_2ClF, we were unable to detect any line broadening of the CH_3 resonances in the \(^1\)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 Farcas.\(^\text{d}\) It would seem clear that there is a substantial medium effect occurring in SO_2ClF. The low boiling point of SO_2ClF makes a quantitative examination at higher temperatures very difficult, and a systematic study was not carried out.

While the highest barrier to stereoemutation of 2 observed here is lower than that reported by Farcas 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 stereoemutation 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 stereoemutation. This means that before we reach a firm conclusion as to the mechanism of the stereoemutation 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.\(^\text{26}\) 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 on the carbocation. Thus, leading to a 8.5 kcal/mol increase of the barrier to inversion.\(^\text{22}\)

A simple way to model the effects of solvation on the stereoemutation barriers of 1 and 2 is achieved by considering a charge-transfer complex between the HOMO energy of the solvent molecule and the LUMO energy of the carbenium ion, and coefficients, eq 1 suggests that the effect of solvation on the two processes has to be considered.\(^\text{27}\) Solvation effects on relative carbocation stabilities are normally considerably smaller and similar in magnitude, however, solvation increases with increasing charge localization as has been demonstrated by Arnott and Petro\(^\text{26}\) for the ionization of alkyl halides in superacid media.

The predictions of this simple model are confirmed by MINDO/3 stabilization energies, \(\Delta H_m\), of RCHOH\(^+\) due to HCl complexation:

\[
\Delta H_m = \Delta H^{\text{SE}}(\text{RCHOH}^+) + \Delta H^{\text{SE}}(\text{HCl}) - \Delta H^{\text{SE}}(\text{HCl}--\text{RCHOH}^+) (2)
\]

For 1, \(\Delta H_m\) 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.\(^\text{20}\)

\(^{26}\text{a}\) All energy values in kilocalories/mole. \(^\text{b}\) This work. \(^\text{c}\) Barrier of CH_3CHC=CHC(OH)CH_3\(^+\), ref 3. \(^\text{d}\) Reference 3. \(^\text{e}\) Atom is sp\(^3\) hybridized. \(^\text{f}\) Atom is sp\(^2\) hybridized. \(^\text{g}\) P, 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 carbocation 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 stereoemutation barrier, we have compared 2 with the \(s\)-isoelectronic allyl cation. Theoretical

\(^{29}\text{MINDO/3 (similar as MINDO) 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 CCl distances are 2.144 (1a), 2.023 (1b), and 2.173 Å (1c). \(\Delta H_m\) 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. In solution phase \( \text{SbF}_5/\text{SO}_2\text{ClF} \), however, the rotational barrier has been estimated to be 10 kcal/mol smaller due to specific solvation at the positive \( C \) atom. 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.

Substituent Effects. The influence of a substituent \( X \) on the stability of the carbenium ion XCHOH* 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 \( \sigma \)

\[
\text{XCHOH}^+ + \text{CH}_2\text{CH}_3 \rightarrow \text{XCH}_2\text{CH}_2 + \text{CH}_3\text{OH}^+ \quad (3)
\]

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

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

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) 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 \( p\) (\( O \)) 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 CO.

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

\[
\text{XCH} = \text{CHCHOH}^+ + \text{CH}_2\text{CH}_3 \rightarrow \text{XCHCH} + \text{CH}_2 = \text{CHCHOH}^+ \quad (4)
\]

- bond character; i.e., the higher the \( \pi \)-donor effect of \( X \), the lower is the \( \text{CO} \) \( \pi \)-bond character. Although our data are limited, we expect that consideration of derivatives of the methoxyacarbemium ions 2 and 18 will lead to lines parallel to the hydroxyacarbemium 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 \( \text{CO} \) 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 XCHOH* 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
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). 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+ is a relatively strong σ donor as in the case of 4, 5, and the protonated acrolesins 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 CICHOCΗ3+ where the experimental barrier to stereomutation is greater than 17.3 kcal/mol (FSO3H/SbF5). 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 π-electron distribution in cations XCHOR+. In 1 and 2 charge is pulled from the OR group (R = H, CH3) toward the positive C atom, thus leading to the relatively high rotational barriers. A nucleophilic solvent molecule or a σ-donor substituent at C* displaces the π cloud to the O atom either by inter- or intramolecular stabilization of the positive charge. In this way, the π character of the CO bond is reduced and rotation is facilitated.

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(32) CICHOCΗ3+, generated in FSO3H/SbF5, shows no averaging of the methyl signals of the two isomers in the 1H NMR spectrum at +50 °C, the temperature at which the cations decompose.