J. Am. Chem. Soc. 1986, 108, 1767-1770

Rearrangement and Dissociative Processes in the $[H_2, C, O]^{\bullet+}$ Potential Energy Surface: An Example of Nonergodic Behavior?

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Abstract: Rearrangement and dissociative processes associated with the formaldehyde ($H_2CO^{\bullet+}$, **1**) and hydroxymethylene ($HCOH^{\bullet+}$, **2**) radical cations have been examined with the aid of ab initio molecular orbital calculations and mass spectrometric experiments. It is predicted theoretically and found experimentally that only HCO^+ (as opposed to HOC^+) ions are generated in the metastable dissociations of $HCOH^{\bullet+}$ and $DCOH^{\bullet+}$. The barriers for the production of $HCO^+ + H^\bullet$ from **2** via direct bond cleavage (183 kJ mol^{-1}) or via rearrangement to **1** followed by fragmentation (179 kJ mol^{-1}) are predicted to be very similar. The kinetic energy release associated with loss of the hydroxyl hydrogen from **2** is substantially greater than that for loss of the originally carbon bound hydrogen, which may result from nonergodic behavior. A third $[H_2, C, O]^{\bullet+}$ isomer, $COH_2^{\bullet+}$, lies 226 kJ mol^{-1} higher in energy than **1** but resides in a potential well of sufficient depth that experimental observation may be feasible.

There has been considerable recent theoretical[2-8] and experimental[9-17] interest in rearrangement and dissociative processes associated with the formaldehyde ($H_2CO^{\bullet+}$, **1**) and hydroxymethylene ($HCOH^{\bullet+}$, **2**) radical cations. It is now well established that **2** is a stable isomer of **1** but separated from it by a substantial barrier. A third possible isomer, the oxonium ion $COH_2^{\bullet+}$ (**3**), has received less attention and has not yet been experimentally observed. The likely stability of **3** is one of the questions addressed here. The main focus of the present paper, however, concerns the relationship between the calculated $[H_2, C, O]^{\bullet+}$ potential surface and metastable transitions, corresponding to $H^\bullet$ loss, observed in the mass spectrometer. Such transitions, as represented by the possible reactions 1–4, have attracted considerable experimental attention, and intriguing results have been obtained for labeled substrates.[9,14,15,17]

$$H_2CO^{\bullet+} \rightarrow HCO^+ + H^\bullet \tag{1}$$

$$HCOH^{\bullet+} \rightarrow HCO^+ + H^\bullet \tag{2}$$

$$HCOH^{\bullet+} \rightarrow COH^+ + H^\bullet \tag{3}$$

$$COH_2^{\bullet+} \rightarrow COH^+ + H^\bullet \tag{4}$$

The approach we use in the present work is a combination of ab initio molecular orbital calculations and mass-spectrometry-based experiments. We explore in detail the $[H_2, C, O]^{\bullet+}$ potential energy surface and tackle in particular the above problems. In the course of our investigation, we find evidence for nonergodic behavior[18] in the metastable decomposition described by reaction 2.

Since the completion of the theoretical calculations described in this paper, a high-quality theoretical study on small $[H_n, C, O]^+$ ions, which includes results for $[H_2, C, O]^{\bullet+}$, has appeared.[19] The focus of that paper was, however, quite different from that of the present study; where the two studies meet, there is good agreement.

Theoretical Approach

Ab initio molecular orbital calculations were carried out with a modified version[20] of the Gaussian 80 system of programs.[21] Geometry optimizations were performed with use of gradient techniques and the split-valence plus *d*-polarization 6-31G* basis set.[22] Improved relative energies were obtained with the *dp*-polarization 6-31G** basis set[22] and with valence-electron correlation incorporated via third-order Møller-Plesset perturbation theory.[23] Vibrational frequencies were calculated at the 4-31G//4-31G level,[24] both to characterize the stationary points

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Table I. Calculated Total Energies (E, hartrees), Relative Energies (ΔE, kJ mol^{-1}), and Zero-Point Vibrational Energies (ZPVE, kJ mol^{-1})

		6-31G*//6-31G*		MP3/6-31G**//6-31G*			
		E	ΔE	E	ΔE	ZPVE	best[a] ΔE
$CH_2{=}O^{\cdot+}$	**1**	-113.52144	0	-113.79977	0	72.0	0
$HC{-}OH^{\cdot+}$	**2**	-113.50367	47	-113.79440	14	72.3	14
$C{-}OH_2^{\cdot+}$	**3**	-113.42268	259	-113.71317	227	71.1	226
TS: **2** → **1**	**4**	-113.41563	278	-113.71993	210	53.2	193
TS: **3** → **2**	**5**	-113.33988	477	-113.64822	398	46.4	375
TS: **1** → $HCO^+ + H^\cdot$	**6**	-113.45276	180	-113.74538	143	48.1	121
TS: **2** → $HCO^+ + H^\cdot$	**7**	-113.42514	253	-113.71613	220	46.1	197
TS: **2** → $HOC^+ + H^\cdot$	**8**	-113.40967	293	-113.69312	280	40.7	252
TS: **3** → $HOC^+ + H^\cdot$	**9**	-113.35347	441	-113.65209	388	47.2	366
$HCO^+ + H^\cdot$		-113.46415	150	-113.75382	121	46.9	98
$HOC^+ + H^\cdot$		-113.41262	286	-113.69676	270	39.7	241

[a] MP3/6-31G**//6-31G* values together with ZPVE correction (scaled by 0.9).

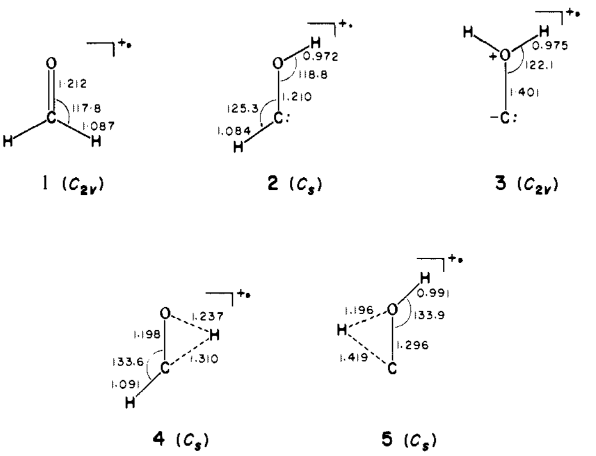

Figure 1. Optimized (6-31G*) equilibrium structures (**1**–**3**) and transition structures for the rearrangement of **2** → **1** (**4**) and of **3** → **2** (**5**).

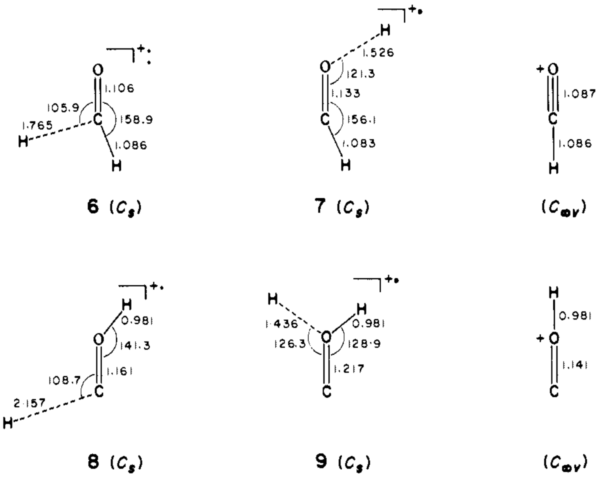

Figure 2. Optimized (6-31G*) transition structures (**6**, **7**) for **1** and **2** → $HCO^+ + H^\cdot$ (reactions 1 and 2) and transition structures (**8**, **9**) for **2** and **3** → $COH^+ + H^\cdot$ (reactions 3 and 4).

as minima (representing equilibrium structures) or saddle points (representing transition structures) and (after scaling by 0.9)[25] to evaluate zero-point vibrational energy corrections to the relative energies.

Calculations were performed on the equilibrium structures $CH_2{=}O^{\cdot+}$ (**1**), $HC{-}OH^{\cdot+}$ (**2**), and $C{-}OH_2^{\cdot+}$ (**3**), the transition structures for rearrangements **2** → **1** (**4**) and **3** → **2** (**5**), and the transition structures (**6**–**9**) for formation of HCO^+ or HOC^+ from **1**, **2**, and **3**.

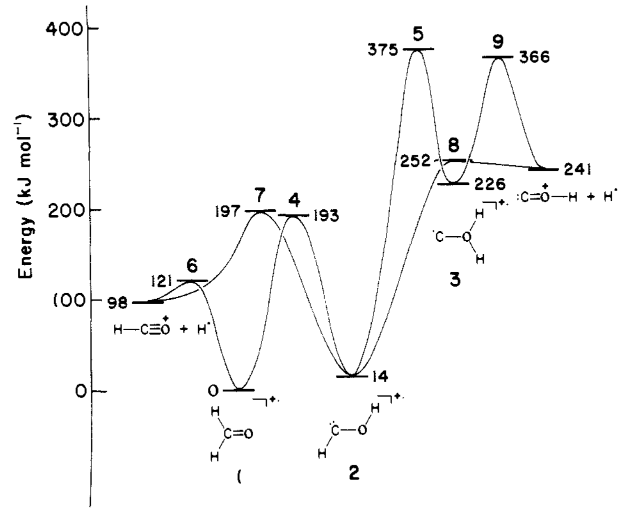

Figure 3. Schematic potential energy surface showing rearrangement and dissociative processes involving $CH_2O^{\cdot+}$ isomers.

Table II. Metastable Peak Characteristics for Hydrogen Loss from $HOCH^{\cdot+}$ Ions[a]

reaction	E_{kin} ($T_{0.5}$, meV)[b,c]
$HCOH^{\cdot+} \rightarrow H^\cdot + HCO^+$ 2 components	400 (14) 150 ± 50 (1)
$DCOH^{\cdot+} \rightarrow H^\cdot + DCO^+$	370 (12)
$DCOH^{\cdot+} \rightarrow D^\cdot + HCO^+$	160 (1)
$HCOD^{\cdot+} \rightarrow H^\cdot + DCO^+$	220 (1)
$HCOD^{\cdot+} \rightarrow D^\cdot + HCO^+$	450 (8)
$DCOD^{\cdot+} \rightarrow D^\cdot + DCO^+$ 2 components	475 (20) 150 ± 50 (1)

[a] From ref 14. [b] Kinetic energy release, ±10 meV, calculated from the peak width at half-height, Kratos MS902S mass spectrometer. [c] Relative abundances are given in parentheses.

Our calculated structures are displayed in Figures 1 and 2 with corresponding energies shown in Table I. A schematic representation of the rearrangement and dissociative reactions in the $CH_2O^{\cdot+}$ surface is shown in Figure 3.

Experimental Approach

In addition to mass spectrometry procedures that have been described previously,[14,26] experiments have been carried out on the Vacuum Generators ZAB-4F mass spectrometer. This is a four-sector instrument with a B E E B configuration (where B and E refer to magnetic and electric sectors, respectively) and is capable of mass spectrometry/mass spectrometry (MSMS) experiments.[27] This allows the identity of the fragment ions resulting from metastable or collisionally induced decompositions to be probed

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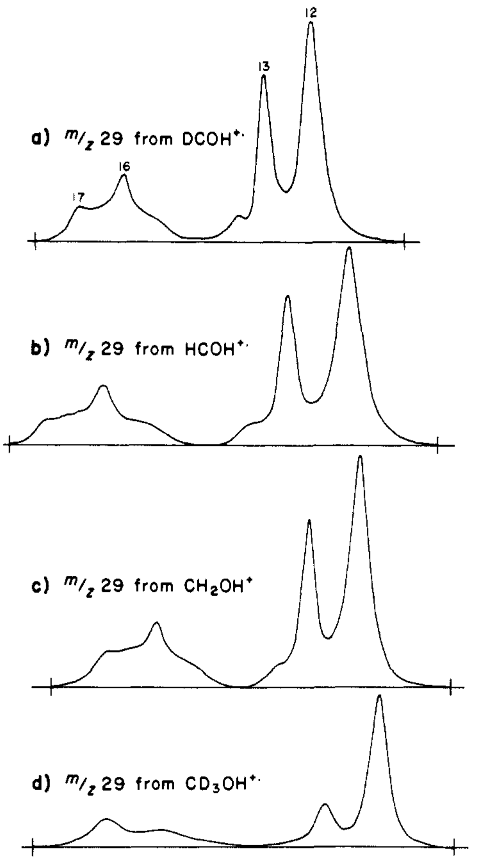

Figure 4. Collisional activation mass spectra of $[C, H, O]^+$ ions produced respectively from (a) $DCOH^{\cdot+}$, (b) $HCOH^{\cdot+}$, (c) H_2COH^+, and (d) $CD_3OH^{\cdot+}$. The spectra in parts a, b, and c are identical and correspond to the HCO^+ ion. The spectrum in part d corresponds to the isomeric HOC^+ ion.

by a second collisional-activation step. Results of such experiments are included in Figure 4 while relevant kinetic energy release data from metastable ion studies[14] are listed in Table II.

Discussion

The potential energy diagram displayed in Figure 3 suggests the existence of three stable $[H_2, C, O]^{\cdot+}$ isomers. The formaldehyde radical cation ($H_2CO^{\cdot+}$, **1**) and the hydroxymethylene radical cation ($HCOH^{\cdot+}$, **2**) are confirmed as low-energy isomers, **2** lying 14 kJ mol^{-1} higher in energy than **1**. The third isomer ($COH_2^{\cdot+}$, **3**) has a high relative energy but lies in a deep potential well. It is separated by a barrier of 149 kJ mol^{-1} from rearrangement to $HCOH^{\cdot+}$ and by a barrier of 140 kJ mol^{-1} with respect to dissociation to $HOC^+ + H^\cdot$. We predict that if a means of generating $COH_2^{\cdot+}$ is devised, this isomer should be sufficiently stable so as to be observable.

The parts of the surface linking **1** and **2** and their dissociation products corresponding to $H^\cdot$ loss may be compared with basic thermochemical data[28] and the more recent information obtained by Burgers, Mommers, and Holmes (BMH).[14] Our results suggest a reinterpretation of some of the BMH data but when this is done, there appears to be generally remarkably good agreement between theory and experiment.

The first point of comparison is the energy difference between $H_2CO^{\cdot+}$ (**1**) and the dissociation products $HCO^+ + H^\cdot$. Our calculated value of 98 kJ mol^{-1} is close to the experimental 92 kJ mol^{-1} (from $\Delta H_f^\circ(H_2CO^{\cdot+}) = 941$, $\Delta H_f^\circ(HCO^+) = 815$, and $\Delta H_f^\circ(H^\cdot) = 218$ kJ mol^{-1}).[26] The agreement between theory and experiment is not as good for the energy of $HCOH^{\cdot+}$ (**2**) relative to $H_2CO^{\cdot+}$ (**1**), theory giving 14 kJ mol^{-1} compared with the experimental value of 45 kJ mol^{-1}. This discrepancy may be due to $HCOH^{\cdot+}$ being formed with excess energy and warrants further attention. Finally, the difference between the appearance energy (AE) of HCO^+ ions formed from CD_3OH (13.05 ± 0.1 eV) and the threshold calculated for HCO^+ (12.8 eV) is 24 kJ mol^{-1} which is very close to the reverse activation energy (23 kJ mol^{-1}) for the dissociation of **1** to $HCO^+ + H^\cdot$ (Figure 3). However, it should be noted that the experimental ionization efficiency curve tailed badly, becoming asymptotic to the energy axis.[14]

Of greater interest are the rearrangement and dissociation processes of the $HCOH^{\cdot+}$ radical cation (**2**). The composite nature of the metastable peak corresponding to loss of $H^\cdot$ suggests the involvement of two different processes for such loss. Through deuterium-labeling experiments, BMH found[14] that the appearance energies for the two processes were the same within experimental error. BMH proposed that the two processes might correspond to production of HCO^+ (reaction 2) and HOC^+ (reaction 3), respectively. The present results do not support such a proposal in that the activation energy calculated for formation of HOC^+ (via **8**) is considerably greater than that for HCO^+ production (via **7**). Instead, our results suggest an alternative rationalization in which both processes involve production of $HCO^+ + H^\cdot$. The first of these is direct O–H bond cleavage and proceeds via transition structure **7**. The second process begins with rearrangement of $HCOH^{\cdot+}$ to $H_2CO^{\cdot+}$ via transition structure **4** and is followed by C–H bond cleavage of the resultant $H_2CO^{\cdot+}$.

Is such a proposal supported by the experimental data? In the first place, the similarity in the calculated activation energies for these two processes (183 kJ mol^{-1} for direct bond cleavage via **7** and 179 kJ mol^{-1} for the rearrangement–fragmentation via **4**) is consistent with the experimental observation that the AE values for metastable $H^\cdot$ and $D^\cdot$ loss from $DCOH^{\cdot+}$ are the same to within experimental error. The experimental AE value (13.9 ± 0.2 eV) corresponds to an energy relative to $H_2CO^{\cdot+}$ of 199 kJ mol^{-1} which is close to the values for **7** and **4** in Figure 3. Moreover, the previous interpretation of this AE in terms of formation of HOC^+ led to an energy for HOC^+ significantly lower than the theoretical value.[31] As is evident from Figure 3, the present interpretation removes this discrepancy.

This theoretical prediction that $DCOH^{\cdot+}$ produces HCO^+ rather than COH^+ was tested by the following experiment. The daughter ions formed in the first field-free region of a VG-ZAB-4F mass spectrometer were transmitted by setting the magnet to the appropriate m/z value (m/z 27.1). It should be noted that the corresponding metastable peak is weak and so background $C_2H_3^+$ ions contribute significantly to the selected ion beam. The $[H, C, O]^+$ ions were separated from the $C_2H_3^+$ ions by adjusting the first electric sector voltage such that only ions having translational energies of $(29/31)V_A$, where V_A is the acceleration voltage, were transmitted by the electric field. Analysis of the $[H, C, O]^+$ ions took place in the third field-free region by collisional activation (CA), and the resulting product ions were energy (mass) analyzed with use of the second electric sector and detected thereafter. The resulting CA mass spectrum is shown in Figure 4a. Figure 4b shows the result of a similar experiment on the unlabeled ion ($HCOH^{\cdot+}$) (mass selection of m/z 28) while the CA mass spectrum of $[H, C, O]^+$ ions generated in the first field-free region from CH_2OH^+, which are known to have the HCO^+ structure, is shown in Figure 4c. For comparison, the CA mass spectrum of COH^+ ions (which are generated in the ion source from CD_3OH) is given in Figure 4d. *It is clear that in these unimolecular dissociations of $HCOH^{\cdot+}$ and $DCOH^{\cdot+}$, only HCO^+ ions are generated.* Note that the double-focussing mass resolution of the first mass spectrometer was necessary to achieve the above result.

The experimental results thus fully support the new theoretical calculations in that only HCO^+ ions are produced from *metastable* $HCOH^{\cdot+}$ ions losing either the carbon bonded *or* the hydroxylic hydrogen atom. The origin of COH^+ is now less certain, but the direct bond cleavage shown in Figure 3 may well take place during fragmentation in the ion source.

Having ascertained that both metastable processes lead to HCO^+ ions, we can now discuss the kinetic energy released in each

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1770 *J. Am. Chem. Soc.* **1986**, *108*, 1770-1775

of these reactions. The results are listed in Table II. For $HCOH^{\bullet+}$ and $DCOD^{\bullet+}$ the metastable peaks are composite, comprising a flat-topped component and a narrower Gaussian-type signal. These can be separated by isotopic substitution.[15] For example, $DCOH^{\bullet+}$ loses $D^{\bullet}$ to produce HCO^{+} (see above) with a small energy release and loses $H^{\bullet}$ to produce DCO^{+} with a large energy release (see Table II).

The kinetic energy release results are also consistent with the theoretical calculations. If we consider the possible fragmentation pathways for $HCOH^{\bullet+}$ that yield $HCO^{+} + H^{\bullet}$, these include direct bond cleavage of the hydroxyl hydrogen (via **7**) and the rearrangement–fragmentation process (via **4**). The first process may be expected to be straightforward and to lead to a considerable amount of energy being converted to translational energy of the fragments. The second process (rearrangement–fragmentation) could lead in the first place to loss of the hydroxyl hydrogen which, in view of the calculated transition structure (**4**), would be a process not dissimilar to the direct loss via **7**. Alternatively, to lose the carbon-bound hydrogen, reaction could proceed via a transient vibrationally excited formaldehyde radical cation.[29] The latter process would allow for more energy to be deposited in internal modes and hence would be expected to occur with a smaller amount of energy converted into translational energy of the fragments. The experimental kinetic energy releases[9,14,15] indeed follow this pattern (Table II): loss of the hydroxyl hydrogen is associated with a much larger kinetic energy release than is loss of the carbon-bound hydrogen. The experimental results for labeled species ($HCOD^{\bullet+}$, $DCOH^{\bullet+}$) demonstrate, in addition, that the rearrangement–fragmentation process may well be nonergodic: the loss of carbon-bound hydrogen (deuterium) with a small kinetic energy release greatly exceeds the same process involving oxygen-bound deuterium (hydrogen). The rearrangement–fragmentation processes for $HCOH^{\bullet+}$ thus bear a resemblance to the methyl loss from the enol form of the acetone molecular ion where there is already strong evidence for nonergodic behavior.[18,30]

Concluding Remarks

The theoretical calculations reported in this paper predict that only HCO^{+} ions are produced in metastable transitions involving $H^{\bullet}$ loss from $HCOH^{\bullet+}$. This prediction is confirmed conclusively through mass-spectrometry-based experiments which examine directly the mestastably generated ions. The measured kinetic energy release for the hydroxyl hydrogen is substantially greater than that for the originally carbon bound hydrogen and may arise from nonergodic behavior.

Acknowledgment. P.C.B. and J.L.H. thank the Natural Sciences and Engineering Research Council of Canada for financial support, the National Institute for Environmental Health Sciences (Research Triangle Park, North Carolina) for access to the VG-ZAB-4F mass spectrometer, and M. M. Bursey and D. J. Harvan for experimental assistance and stimulating discussions.

Registry No. 1, 54288-05-0; **2**, 63541-95-7; **3**, 74236-24-1.

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[29] Note that although formaldehyde molecular ions do lose $H^{\bullet}$ close to the thermochemical threshold for HCO^{+} formation, it has been concluded[17] that in the metastable (μs) time frame, fragmentation takes place from the excited A $^2B_1$ state at an energy which lies ca. 310 kJ mol^{-1} above the ground X $^2B_2$ state of $H_2CO^{+\bullet}$. Formation of HOC^{+} from the excited state is thermochemically feasible in principle (see Figure 3) via an isomerization to $HCOH^{+\bullet}$. However, we could find no experimental evidence for production of HOC^{+} from ionized formaldehyde and so conclude that there may be an energy barrier for the rearrangement reaction.

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[31] **Note Added in Proof**: Since submission of this manuscript, a new experimental estimate of 152 kJ mol^{-1} has been reported (McMahon, T. B.; Kebarle, P. *J. Chem. Phys.* **1985**, *83*, 3919) for the energy difference between HOC^{+} and HCO^{+}. This is close to the theoretical value of 157 kJ mol^{-1} (Nobes, R. H.; Radom, L. *Chem. Phys.* **1981**, *60*, 1) and therefore provides additional support for the conclusions of the present paper.

A Simple Method for Calculating Atomic Charge in Molecules

John Mullay

Contribution from the Atlas Powder Company, Tamaqua, Pennsylvania 18252.
Received July 12, 1985

Abstract: Atomic charges are calculated by using a bond orbital electronegativity method which was developoed previously to estimate group electronegativity. For any molecule or radical containing N different bonds the method requires the solution of N simultaneous equations which are linear in orbital charge. Input data required are the following: an effective nuclear charge for each atom (from modified Slater's rules), an effective principal quantum number (also from Slater rules), percent p character of the atomic orbitals used in the bonds, an estimate of the bond order for each bond, and an estimate of the effective number of electrons in each bonded atomic orbital prior to bonding (between 0 and 2). The flexibility of the method allows the bonding information to be obtained from either classical or resonance theory. It also allows for the treatment and analysis of simple or complex bonding situations. Results from this method are compared to both ESCA data and theory (Mulliken and Politzer procedures). It is shown that the method reproduces results obtained from the more sophisticated theoretical methods as well as correlating very well with experiment. It is also shown that the method can be used to provide insights into details of the electronic charge distributions in molecules.

The concept of atomic charge is one that has continued to elude attempts at clear and unambiguous definition.[1,2] However it remains very useful to chemists.[1,3-10] As a result there have been various attempts made to obtain both calculated and measured values.[1,11-15] Lately significant efforts have been made in both

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