

maximal for tight transition-state reactions such as the  $\text{CH}_3 + \text{CH}_4$  system and to diminish as the transition state becomes more loose and the reacting moieties become more complex. Static solvent caging effects are much less pronounced in typical isomerizations. Nonetheless, pressure variation of the activation volume can play an important role in the elucidation of dynamic solvent effects on rates.

**Acknowledgment.** B.M.L. acknowledges support of this work by NSF Grant CHE84-05165. Computational work was supported by NIH Grant GM27945. Acknowledgment is made by J.T.H. to the Donors of the Petroleum Research Foundation, administered by the American Chemical Society, for partial support of this work. J.T.H. also acknowledges support by NSF Grants CHE81-13240 and CHE84-19830.

## Substituent Effects on Neutral and Ionized C=C and C=O Double Bonds and Their Implications for the Stability Order of Keto/Enol Tautomers

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**Abstract:** By using ab initio molecular orbital (MO) calculations substituent effects on monosubstituted neutral as well as cationic ethylene and formaldehyde are studied. The relative stabilizations caused by substitution have been evaluated by means of isodesmic reactions employing a complete "first row sweep". The so-obtained results have been used to investigate the relative stabilizations of simple, substituted neutral and cationic keto/enol pairs.  $\pi$ -donating and -accepting as well as  $\sigma$ -accepting substituents were found to stabilize the neutral C=C bond thermochemically. The C=O double bond is highly stabilized by  $\pi$ -donating and  $\sigma$ -accepting substituents, and the stabilization effects are much larger compared to those found for the corresponding C=C double bond systems. Substantial stabilization is provided by a strong polarization of the double bond. Substituents which are able to reinforce an already existing bond polarization are stabilizing most efficiently. In the cationic species, the ability of the substituent to donate negative charge, thereby compensating the electron deficiency caused by ionization, is found to be of prime importance. Both  $\sigma$ - and  $\pi$ -donors provide substantial stabilization. The relative stabilizations for C=O double bond containing cationic species are smaller for  $\pi$ -donating groups and larger for  $\sigma$ -donors compared to the corresponding cationic ethylene derivatives. These findings also apply for neutral and ionized acetaldehyde and vinyl alcohol derivatives. The effect on the respective keto/enol energy differences is discussed.

It is well-known that simple noncrowded neutral ketones, aldehydes, and carboxylic acids are, in general, thermochemically and kinetically more stable than their corresponding enol forms.<sup>1</sup> However, for the cation radicals of keto/enol pairs a reversal of the stability order is observed. The enol form usually turns out to be the more stable tautomer as shown by both experiment<sup>2</sup> and theory.<sup>3</sup> The energy difference between neutral and charged keto/enol pairs is highly dependent upon the electronic properties of the substituent attached directly to the C=O or C=C double bond, respectively. Obviously, the understanding of substituent effect on C=C and C=O double bonds in neutral or charged molecules is a prerequisite for explaining the remarkable effects observed for the keto/enol pairs. In this paper we report on our results of ab initio molecular orbital (MO) calculations on monosubstituted neutral and cationic ethylene and formaldehyde derivatives in order to rationalize the effect of a substituent in terms of its electronic properties. The effect of substituents located at the  $\alpha$ -carbon atom of neutral and cationic vinyl alcohol and acetaldehyde are analyzed in a systematic way<sup>4</sup> by means of isodesmic reactions.<sup>5</sup> Additional work concerning the substituent effects on the transition states for the interconversions of keto/enol tautomers, which are highly affected by the nature of a substituent, is in progress and will be published elsewhere.<sup>6,7</sup> For a thorough study of substituent effects we employed a complete "first row sweep", and the substituents that were chosen, i.e., F, OH,  $\text{NH}_2$ ,  $\text{CH}_3$ ,  $\text{BH}_2$ , and BeH, encompass a wide range of electronic properties.<sup>4</sup> F is a strong  $\sigma$ -acceptor and a weak  $\pi$ -donor; both OH and  $\text{NH}_2$  are strong  $\pi$ -donors but weaker  $\sigma$ -acceptors.  $\text{CH}_3$

exerts much milder electronic effects, being capable of acting either as a  $\pi$ -donor or  $\pi$ -acceptor and, additionally, as a weak  $\sigma$ -donor.

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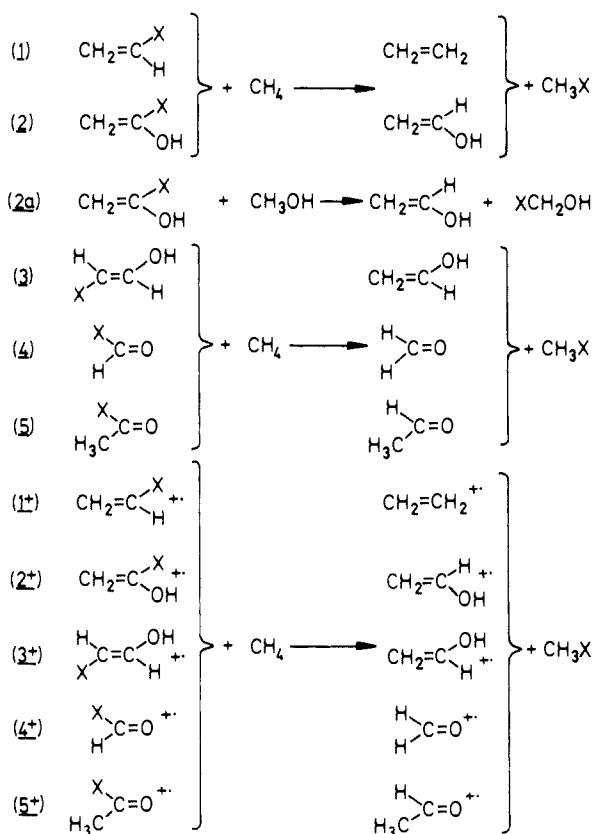
\* Present address: SRI International, Menlo Park, CA 94025.

Table I. Calculated Total Energies (hartrees) for HF/6-31G\*\*/3-21G Optimized Structures

a. 1-5					
substituent X	1	2	3	4	5
H	-78.03168	-152.88754	-152.88754	-113.86524	-152.91335
F	-176.88082	-251.74430	-251.72567	-212.74619	-251.79510
OH	-152.88754	-227.75189	-227.72763	-188.76006	-227.80855
NH <sub>2</sub> (planar)	-133.05905	-207.92217	-207.89988	-168.92994	-207.97511
NH <sub>2</sub> (perpend)	-133.04354	-207.90664	-207.89722	-168.8894	-207.93232
CH <sub>3</sub>	-117.07147	-191.93099	-191.92113	-152.91335	-191.95772
BH <sub>2</sub> (planar)	-103.28962	-178.14231	-178.15596	-139.10657	-178.15089
BH <sub>2</sub> (perpend)	-103.27715	-178.13039	-178.13126	-139.11051	-178.15788
BeH	-92.65861	-167.51150	-167.52152	-128.49514	-167.54704

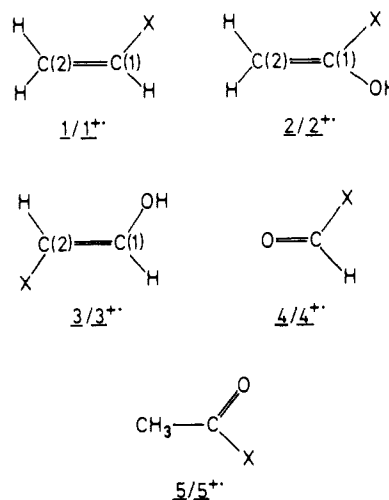
  

b. 1 <sup>+</sup> -5 <sup>+</sup>					
substituent X	1 <sup>+</sup>	2 <sup>+</sup>	3 <sup>+</sup>	4 <sup>+</sup>	5 <sup>+</sup>
H	-77.71229	-152.60389	-152.60389	-113.52037	-152.59133
F	-176.56063	-251.45505	-251.43796	-212.35559	-251.43283
OH	-152.60389	-227.49585	-227.47456	-188.40696	-227.47769
NH <sub>2</sub> (planar)	-132.82368	-207.69505	-207.68160	-168.61704	-207.66168
NH <sub>2</sub> (perpend)	-132.74483	-207.63286	-207.60807	-168.54039	-207.58671
CH <sub>3</sub>	-116.77184	-191.66350	-191.65501	-152.59133	-191.65592
BH <sub>2</sub> (planar)	-102.96478	-177.85610	-177.86164	-138.78565	-177.84797
BH <sub>2</sub> (perpend)	-102.97406	-177.86102	-177.86015	-138.79670	-177.86172
BeH	-92.35284	-167.23959	-167.24264	-128.18407	-167.24698

Scheme I. Isodesmic Reactions 1-5 and 1<sup>+</sup>-5<sup>+</sup> neutr./rad. cat.

In contrast, BH<sub>2</sub> and BeH are strong  $\pi$ -acceptors and  $\sigma$ -donors. For completion we had originally included Li as well which is

Chart I



known as a powerful  $\sigma$ -donor but a weak  $\pi$ -acceptor; however, the tendency of Li to form bridged hypervalent structures<sup>8</sup> did not permit us to make a complete, detailed comparison of the electronic changes in the molecular skeleton of lithiated species with the effects observed for the more conventional structures obtained for all other first row substituents. Thus, the effects of Li will not be discussed in this paper. In order to evaluate the relative energies of stabilization/destabilization caused by a substituent X we performed several isodesmic reactions as shown in Scheme I.

The choice of the reference system for calculating stabilization energies is necessarily somewhat arbitrary and one has to evaluate carefully which effects are due to the reference system, which in our case is CH<sub>4</sub>/CH<sub>3</sub>X. The  $\sigma$ - and  $\pi$ -interactions in monosub-

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**Table II.** Theoretical (HF/6-31G\*/3-21G) and (in Parentheses) Experimental Heats of Reaction,  $\Delta H_r^\circ$ , for the Isodesmic Reactions 1-5<sup>a</sup>

substituent X	1	2	2a	3	4	5
F	6.9 (6.2) <sup>a</sup>	11.7	-0.8 <sup>e</sup>	0.0	26.9 (22.3) <sup>f</sup>	27.4
OH	10.9 (11.2) <sup>b</sup>	16.2	0.9 <sup>e</sup>	0.9	35.3 (32.3) <sup>d</sup>	35.6
NH <sub>2</sub> (planar)	8.0 (5.4) <sup>c</sup>	12.6		-1.5	31.5 (28.9) <sup>g</sup>	29.6
NH <sub>2</sub> (perpend)	-1.7	2.8		-3.1	6.0	2.7
CH <sub>3</sub>	4.0 (5.2) <sup>d</sup>	6.3		0.1		6.9
BH <sub>2</sub> (planar)	7.3	5.3		13.9	-3.2	-5.5
BH <sub>2</sub> (perpend)	-0.5	-2.2		-1.7	-0.7	-1.2
BeH	3.9	2.0		8.3	5.7	8.1

<sup>a</sup>Kolesov, V. P.; Papina, T. S. *Zh. Fiz. Khim.* **1970**, *44*, 1101. <sup>b</sup>Estimated by using ref 31 and 33. <sup>c</sup>Estimated by taking experimental  $\Delta H_r^\circ$  (ethylene imine\*) from ref 31, the calculated energy difference ethylene imine\*/vinyl amine\* (-30.4 kcal/mol; HF/6-31G\*/3-21G) and  $E_{ad}$  from ref 34. <sup>d</sup>Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1970. <sup>e</sup>Whiteside, R. A.; Frisch, M. J.; Pople, J. A. "Carnegie Mellon Quantum Chemistry Archive", 3rd ed.; 1983. <sup>f</sup>Stull, D. R.; Prophet, J. "JANAF Thermochemical Tables", 2nd ed.; U.S. Government Printing Office: Washington, D.C., 1971; NSRDS-NBS. <sup>g</sup>Benson, S. W.; Rodgers, A. S.; Walsh, R. *Chem. Rev.* **1969**, *69*, 279. <sup>h</sup>Calculated total energies (HF/6-31G\*/3-21G) of the species used for the reference system (in hartrees): CH<sub>4</sub>, -40.19517; CH<sub>3</sub>F, -139.03333; CH<sub>3</sub>OH, -115.03376; CH<sub>3</sub>NH<sub>2</sub>, -95.20983; CH<sub>3</sub>CH<sub>3</sub>, -79.22861; CH<sub>3</sub>BH<sub>2</sub>, -65.44153; CH<sub>3</sub>BeH, -54.81593. Energies are given in kcal/mol.

**Table III.**  $\pi$ - and  $\sigma$ -Charge Transfer from the Substituent X into the Double Bond (Neutral Species)

X	1		2		3		4		5	
	$\pi$	$\sigma$	$\pi$	$\sigma$	$\pi$	$\sigma$	$\pi$	$\sigma$	$\pi$	$\sigma$
F	+0.04	-0.43	+0.03	-0.39	+0.02	-0.41	+0.06	-0.41	+0.09	-0.46
OH	+0.08	-0.36	+0.06	-0.32	+0.05	-0.34	+0.12	-0.34	+0.11	-0.35
NH <sub>2</sub> (planar)	+0.12	-0.28	+0.10	-0.25	+0.08	-0.25	+0.17	-0.27	+0.15	-0.26
NH <sub>2</sub> (perpend)	+0.01	-0.22	-0.01	-0.17	-0.01	-0.19	+0.02	-0.18	+0.03	-0.22
CH <sub>3</sub>	+0.01	+0.01	-0.01	+0.06	-0.01	+0.03	+0.01	0.00	+0.03	-0.01
BH <sub>2</sub> (planar)	-0.18	+0.27	-0.10	+0.21	-0.14	+0.19	-0.03	+0.20	-0.02	+0.18
BH <sub>2</sub> (perpend)	-0.02	+0.18	-0.02	+0.10	-0.03	+0.18	0.00	+0.18	+0.02	+0.15
BeH	-0.08	+0.25	-0.06	+0.25	-0.10	+0.25	-0.02	+0.25	-0.06	+0.17
H		+0.18		+0.20		+0.20		+0.15		+0.15

stituted methanes have already been described in detail by other groups.<sup>9</sup> Thus, the  $\Delta H_r^\circ$  values obtained by our isodesmic reactions are a measure of additional  $\sigma$ - and  $\pi$ -interactions which are present when the substituent is attached to a double bond but not to a methyl group.

### Computational Details

Standard ab initio MO calculations have been performed by using a modified version of the GAUSSIAN 76 series of programs<sup>10</sup> which includes the Davidson-Fletcher-Powell multiparameter search<sup>11</sup> with analytically evaluated gradients.<sup>12</sup> Geometry optimizations were carried out with the split-valence 3-21G<sup>13</sup> basis set while single point calculations were performed at the d-polarized 6-31G\*<sup>14</sup> level; the latter calculations will be denoted as HF/6-31G\*/3-21G. All open-shell structures have been treated with the unrestricted Hartree-Fock (UHF) formalism.<sup>15</sup> Calculations were done on the CRAY-1M computer at the Konrad-Zuse-Zentrum für Informationstechnik, Berlin.

### Results and Discussion

The total energies at 6-31G\* for the species mentioned in reactions 1-5 and 1<sup>+</sup>-5<sup>+</sup> (Scheme I) are presented in Table I (parts a and b). (See Chart I.) The calculated energies for the isodesmic reactions given in Scheme I are listed in Tables II and V. Positive  $\Delta H_r^\circ$  values correspond to a relative stabilization of the left-hand side of the equations. It should be mentioned that in these reactions cancellation of errors due to electron correlation effects can be expected.<sup>5</sup> Thus substituent effects in nonbridged structures should be described reasonably well even at 6-31G\*.<sup>16</sup> The

agreements of our calculated heats of reaction  $\Delta H_r^\circ$  with those obtained by using experimental heats of formation are, indeed, in most cases satisfying. Note that the  $\Delta H_r^\circ$  values based on 3-21G energies are usually somewhat higher but follow the same trend predicted by 6-31G\*. Geometries calculated with 3-21G are known to be of approximately equal quality to 4-31G level structures and often superior in evaluating bond lengths.<sup>17</sup> The 3-21G basis set offers, however, a significant computational advantage in the evaluation of energy derivatives and the energy itself and is well-suited for even larger molecules. The  $\sigma$ - as well as  $\pi$ -charge transfers induced by the substituent X into the respective double bond containing moiety compared to the unsubstituted system are given in Tables III and VI. These data have been calculated by using the 6-31G\*-Mulliken populations.

**1. Neutral Systems. A. Substituent Effects on C=C and C=O Double Bond Containing Molecules.** The results for the isodesmic reaction 1 reveal that F, OH, NH<sub>2</sub>(planar),<sup>18</sup> and BH<sub>2</sub>(planar) stabilize the ethylene system effectively. The stabilization differences found for the perpendicular arrangement of NH<sub>2</sub> and BH<sub>2</sub> clearly indicate the importance of  $\pi$ -conjugation in both cases. The stabilization due to hyperconjugation<sup>19</sup> between the  $\pi_{\text{NH}_2}$  and  $\pi_{\text{C-C}}$  orbital in the perpendicular species is negligibly small. NH<sub>2</sub>(planar) and BH<sub>2</sub>(planar) are stabilizing by 8.0 and 7.3 kcal/mol, respectively, for the perpendicular NH<sub>2</sub> and BH<sub>2</sub> even

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(18) Note, however, that a planar equilibrium geometry for vinyl amine is due to a 3-21G basis set deficiency. There is experimental as well as theoretical evidence for a slight pyramidalization in the NH<sub>2</sub> group. See: (a) Lovas, F. J.; Clark, F. O. *J. Chem. Phys.* **1975**, *62*, 1925. (b) Saeko, S.; Radom, L. *J. Mol. Struct.* **1983**, *105*, 119. Furthermore, all HF calculations strongly indicate a planar structure for ethylene cation radical despite experimental evidence for a slight twisting, whereas for substituted ethylene cation radicals, such as vinyl amine and vinyl alcohol, the theoretically predicted planar structure is in agreement with experimental findings. See: (c) Handy, N. C.; Nobes, R. H.; Werner, H.-J. *Chem. Phys. Lett.* **1984**, *110*, 459. (d) See also ref 31 and 34.

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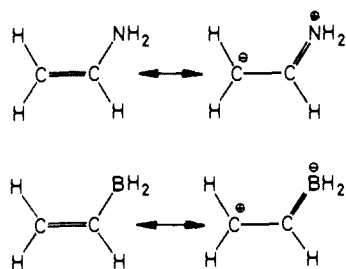
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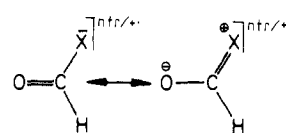
Chart II



a slight destabilization of  $-1.7$  and  $-0.5$  kcal/mol was found, respectively. Thus, both  $\pi$ -donation and  $\pi$ -acceptance stabilize a  $C=C$  double bond system thermochemically. However, since the stabilization found for OH is even larger by 10.9 kcal/mol than for  $NH_2$ (planar),<sup>20</sup> it follows that  $\sigma$ -acceptance also exerts a stabilizing effect. The stabilization caused by fluorine (6.9 kcal/mol) is likely to be due to the less pronounced  $\pi$ -donor ability of F (compared to OH and  $NH_2$ ) and its role as a strong  $\sigma$ -acceptor. BeH exhibits less stabilization compared to  $BH_2$ (planar) because of weaker  $\pi$ -acceptance. The methyl group is stabilizing only by 4.0 kcal/mol because of its weak  $\pi$ - and  $\sigma$ -interactions. The different effects caused by the substituent used are reflected in the charge distributions,  $p_y$ -(out-of-plane)-orbital populations, and the  $\sigma$ -/ $\pi$ -transfer shown in Table III. As expected,  $\pi$ -interacting substituents effect mostly the  $p_y$ -orbital population at the terminal carbon atom  $C_{(2)}$ . For  $NH_2$ (planar) the  $C_{(2)}$ - $p_y$ -orbital population is increased from 0.99 e (for ethylene) up to 1.20 e. In contrast, for  $BH_2$ (planar) the lowest  $p_y$ -orbital population of 0.82 e is found reflecting its strong  $\pi$ -acceptor ability and indicating the contribution of the resonance structures shown in Chart II. Due to the increased  $\pi$ -character, the C-N and C-B bonds in vinyl amine and vinyl borane are shortened by 0.093 and 0.028 Å, respectively, compared to the corresponding bonds in substituted methanes (1.472 and 1.577 Å, respectively). Equivalently, this can also be explained in terms of changing the hybridization from  $sp^3$  to  $sp^2$  at  $C_{(1)}$  and thus changing the  $\pi$ -donor/-acceptor properties. Experimental evidence for the  $\pi$ -character in the C-O bond in vinyl alcohol is found in the torsional frequency of the OH group which lies between that for saturated alcohols and carboxylic acids.<sup>21</sup> A further source of stabilization is due to the ability of the substituent to polarize the molecular skeleton, resulting in stabilizing attractive Coulomb interaction. As the polarization is directly related to the electron withdrawal ability of the substituent, it will be diminished with decreasing electronegativity. Thus, the polarization and thereby the degree of ionicity in the C-C bond decreases in the order  $F > OH > NH_2 > CH_3 > BH_2 > BeH$ . The C-C bond lengths parallel this effect.

How do the substituent effects alter the thermochemical stabilities when the nearly nonpolar  $C=C$  double bond is replaced by the strongly polar  $C=O$  double bond? The isodesmic reactions 4 (Scheme I, Table II) reveal two effects. Firstly, the stabilization ability order of the substituent is, except for  $BH_2$ , the same as found for reaction 1; however, the magnitudes of the effects are drastically enhanced in the carbonyl series. Again,  $\pi$ -donors are strongly stabilizing. The comparison of planar and perpendicular  $NH_2$  clearly demonstrates the contribution from  $\pi$ -resonance which is much more effective than in the corresponding substituted ethylenes since the  $C=O$  double bond is a strong  $\pi$ -acceptor compared to the  $C=C$  double bond. For example, the difference in stabilization of  $NH_2$ (planar) vs.  $NH_2$ (perpendicular), which approximately represents the  $\pi$ -contributions, amounts to 25.5 kcal/mol in the formyl system and is dropped to 9.7 kcal/mol in the ethylene system. The  $\pi$ -electron transfer of 0.12 e from the planar substituent into the  $C=C$  double bond is increased to 0.17

Chart III



e in the  $C=O$  double bond system comparing the data in Table III.

Secondly, in contrast to the substituted ethylenes, strong  $\pi$ -acceptors like  $BH_2$ (planar) destabilize the carbonyl compounds. As a consequence, the perpendicular formyl borane is more stable than the polar conformer which indicates that in contrast to the substituted ethylenes the direction of  $\pi$ -interaction evidently plays a decisive role in the highly polarized system. A  $\pi$ -donor substituent stabilizes, whereas a  $\pi$ -acceptor destabilizes the C-O double bond. The effect of  $\pi$ -donation on the C-O moiety should be indicated by a lengthening of the C-O bond reflecting the contribution of the resonance structures shown in Chart III.

In fact, with respect to the C-O bond length of 1.207 Å in formaldehyde, for  $NH_2$ (planar) a marginal elongation of 0.005 Å could be found. F and OH, although being  $\pi$ -donors, cause a substantial bond shortening of 0.027 and 0.009 Å, respectively, which is due to the reinforced Coulomb attraction in the C-O moiety. Thus, structural distortions are more related to effects of the  $\sigma$ -electronegativity rather than to  $\pi$ -donor/-acceptor properties. Very similar conclusions have been drawn by Domenicano et al.<sup>22</sup> and, in particular, Apeloig et al.<sup>4b</sup> in a recent paper reporting on substituent effects on  $C=Si$  double bonds. Both effects,  $\pi$ -donation and  $\sigma$ -acceptance, lead to large charge alternation which explains the most efficient stabilization by OH being both a good  $\pi$ -donor and  $\sigma$ -acceptor. The data from Table III show that the  $\pi$ -donation from the OH group is more effective in formic acid (0.12 e) than it is in vinyl alcohol (0.08 e) due to the stronger polarization of the multiple bond in the formyl system. This interpretation is in good agreement with the observed vibrational frequencies of the OH torsion in formic acid vs. vinyl alcohol (638  $cm^{-1}$  vs. 413  $cm^{-1}$ , respectively).<sup>21a</sup> The BeH-substituted formyl system already shows an oxygen-bridged structure ( $\angle HCB_e = 180^\circ$ ) which is also known for lithiated species. In addition, we have calculated the bent structure ( $\angle HCB_e = 119^\circ$ ), the latter being 8.4 kcal/mol less stable than the former bridged one. A comparison of the charge distribution of the two species indicates the strong back-donation in the bridged structure: the  $p_y$ -population on Be increases from 0.02 to 0.07 e accompanied by a strong increase of the  $\sigma$ -charge from +0.25 to +0.42. In the bent structure, the BeH group slightly destabilizes the carbonyl function ( $-2.7$  kcal/mol) which is mainly due to Coulombic repulsion of the BeH and HCO units. A decreased polarization of the C-O bond causes an elongation of this bond by 0.026 Å, compared to formaldehyde, which is not related to conjugative effects as indicated by nearly identical  $p_y$ -orbital populations on oxygen for X = BeH (1.31 e) and X = H (1.30 e). Conclusions, essentially in line with the ones reported here, were recently described by Greenberg and Stevenson by using ab initio calculations to describe substituent effects on neutral ethylene derivatives.<sup>35</sup>

**B. Substituent Effects on Keto/Enol Pairs.** We investigated the substituent effects on the relative stabilities of neutral vinyl alcohol attached at either  $C_{(1)}$  or  $C_{(2)}$  (trans) (i.e., species 2 and 3), respectively, and acetaldehyde derivatives substituted on the carbonyl C-atom (i.e., species 5). All isodesmic processes are again related to the reference system  $CH_4/CH_3X$ . Reactions 2 and 3 were interpreted throughout in terms of the planar syn-conformer of vinyl alcohol which turns out to be 2.2 kcal/mol (HF//6-31G\*/3-21G) more stable than the anti conformer, in line with experimental findings.<sup>23</sup> The data from the isodesmic reaction

(20) We note that the substantially enhanced reactivity of electron-rich ethylene derivatives like vinyl alcohol or vinyl amine has to be seen as a consequence of their kinetic instability. From a thermochemical point of view ethylene becomes stabilized when functionalized by OH or  $NH_2$ .

(21) (a) Hawkins, M.; Andrews, L. *J. Am. Chem. Soc.* **1983**, *105*, 2523. (b) Rodler, M.; Blom, C. E.; Bauder, A. *Ibid.* **1984**, *106*, 4029.

(22) Domenicano, A.; Murray-Rust, P.; Vacic, A. *Acta Crystallogr., Sect. B: Struct. Sci.* **1983**, *B39*, 457.

(23) (a) Samdal, S.; Seip, H. M. *J. Mol. Struct.* **1973**, *35*, 193. (b) Saito, S. *Chem. Phys. Lett.* **1976**, *42*, 399. (c) Bouma, W. J.; Radom, L. *J. Mol. Struct.* **1978**, *43*, 267. (d) Capon, B.; Siddhanta, A. K. *J. Org. Chem.* **1984**, *49*, 255. (e) Rodler, M.; Bauder, A. *J. Am. Chem. Soc.* **1984**, *106*, 4025.

2 (Table II) show that the stability order for the neutral substituted vinyl alcohols is nearly the same as for the substituted ethylenes (reaction 1).  $\pi$ -Conjugation again is the dominant stabilizing factor as demonstrated by comparing the planar and perpendicular arrangements for  $\text{NH}_2$  and  $\text{BH}_2$ , the planar conformers being more stable by 9.8 and 7.5 kcal/mol, respectively. However, the stabilization by  $\pi$ -donors is enhanced whereas the effect of  $\pi$ -acceptors is weakened compared to reaction 1. This is reasonable since in the geminal substituted vinyl alcohol derivatives the substituent is now located at the carbon atom  $\text{C}_{(1)}$  which is electron deficient due to the electron withdrawal by OH. Thus the C=C double bond in vinyl alcohol may be considered as in between that for the "nonpolar" ethylene and the highly polarized carbonyl group, and the results are in line with this picture.

The direction of the  $\pi$ -effects is well-reflected by the differences in the  $p_y$ -orbital populations at  $\text{C}_{(1)}$  and  $\text{C}_{(2)}$ .  $\pi$ -Donation by  $\text{NH}_2$ (planar) results in a highly polarized C-C- $\pi$  bond. The  $p_y$ -orbital population at the terminal C-atom  $\text{C}_{(2)}$  is remarkably increased from 1.15 e in vinyl alcohol to 1.33 e in 1,1-amino-hydroxyethylene whereas a strong decrease at  $\text{C}_{(1)}$  from 0.91 to 0.82 e is found. The difference in the  $p_y$ -populations representing the polarization of the  $\pi$ -system amounts to 0.51 e. For  $\text{BH}_2$ (planar) the difference in the  $p_y$ -populations of 0.12 e is rather small: the  $p_y$ -population at  $\text{C}_{(2)}$  has dropped to 1.04 e whereas the value for  $\text{C}_{(1)}$  remains roughly unchanged compared to vinyl alcohol.  $\text{BH}_2$  diminishes the polarization of the C-C- $\pi$  bond whereas  $\text{NH}_2$  reinforces this polarization. It should be noted that the  $\pi$ -effects are additive: the  $\pi$ -population in the C-C bond is approximately obtained by combining the  $\pi$ -distribution in the C-C bond of the respective parent systems, i.e., the monosubstituted ethylenes. The  $\sigma$ -framework in vinyl amine is polarized toward  $\text{C}_{(2)}$  whereas a reverse polarization was found for vinyl borane, the former ( $\Delta\sigma_{\text{C-C}} = 0.82$ ) being somewhat stronger than the latter ( $\Delta\sigma_{\text{C-C}} = -0.64$ ). In terms of these arguments it is somewhat surprising that for  $\text{X} = \text{BH}_2$  a C=C bond length of 1.327 Å was found being as large as for  $\text{X} = \text{NH}_2$ . Stabilization also arises from  $\sigma$ -acceptance by substituents like F and OH, and the effect is enlarged compared to reaction 1. For F, for example, the changes in the  $\pi$ -framework are rather moderate; however, the positive total charge on  $\text{C}_{(1)}$  is drastically increased from +0.22 in vinyl alcohol to +0.79 in 1,1-fluorohydroxyethylene. Accounting for the small  $\pi$ -electron transfer of +0.03 e by F (see Table III), the remaining difference of -0.39 to the total charge on F has to be assigned to withdrawal effects in the  $\sigma$ -framework by diminishing the  $\sigma$ -population on  $\text{C}_{(1)}$ . The small increase in the total population at  $\text{C}_{(2)}$  is exclusively due to the weak  $\pi$ -donation by F. Thus, stabilization by F is predominately due to strong polarization of the  $\sigma$ -framework. According to the  $\Delta H_f^\circ$  values of reactions 1, 2, and 4, it can be concluded that with increasing polarization of the parent system the stabilization by  $\pi$ -donor/ $\sigma$ -acceptor substituents also increases. For example, OH stabilizes ethylene by 10.9 kcal/mol, vinyl alcohol by 16.2 kcal/mol, and formaldehyde even by 35.3 kcal/mol. In order to sort out electrostatic and  $\pi$ -resonance effects of the electronegative substituents we have changed the reference system for the isodesmic reaction from  $\text{CH}_4/\text{CH}_3\text{X}$  (reaction 2, Scheme I) to  $\text{CH}_3\text{OH}/\text{XCH}_2\text{OH}$  (reaction 2a, Scheme I) for  $\text{X} = \text{F}$  and OH. It has been reported<sup>9d,24,25</sup> that geminal disubstitution by two electronegative groups results in a high stabilization due to electrostatic and/or hyperconjugative effects. The fact that the energies for the reaction 2a are close to zero indicates that there is no additional stabilization in geminal disubstituted ethylenes relative to the disubstituted methanes. These effects are well-reflected by the C-O and C-F bond lengths, depicted in Chart IV, which are substantially shortened compared with vinyl alcohol and vinyl fluoride, respectively. Similar arguments explain the stabilizing effects of substituents attached to  $\text{C}_{(2)}$  in vinyl alcohol (species 3). However, according to the  $\Delta H_f^\circ$  values (Table II) for the isodesmic reaction 3, no significant stabilization arises from  $\pi$ -

Chart IV

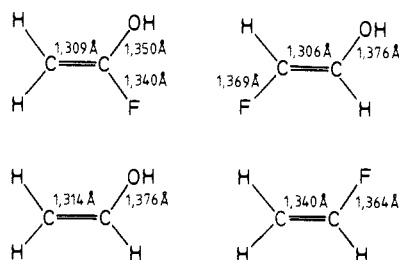
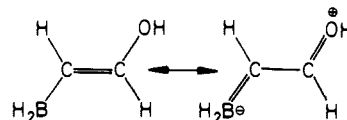


Chart V



donating groups. For example, OH attached at  $\text{C}_{(2)}$  stabilizes only by 0.9 kcal/mol whereas for  $\text{NH}_2$ (planar) even a slight destabilization of -1.5 kcal/mol was found. The distribution of  $\pi$ -electrons in the C-C moiety is balanced (for example, for  $\text{X} = \text{NH}_2$ (planar):  $p_y(\text{C}_{(1)}) = 1.09$  e;  $p_y(\text{C}_{(2)}) = 1.03$  e) since donation by OH and the substituent X operate "out-of-phase". For  $\pi$ -donor/ $\sigma$ -acceptor substituents it holds that the combined  $\sigma$ - and  $\pi$ -effects of OH and X nearly cancel each other. Remarkable stabilization is found only for  $\pi$ -accepting groups like  $\text{BH}_2$ (planar): here,  $\pi$ -donation by OH and  $\pi$ -acceptance by  $\text{BH}_2$  (or BeH) operate "in phase" resulting in synergetic stabilization ("push-pull"-effect) which is 13.9 kcal/mol for  $\text{BH}_2$ . As a consequence, the C-C bond is lengthened by 0.022 Å compared to vinyl alcohol ( $r_{\text{C-C}} = 1.314$  Å). The C-O and C-B bonds are shortened by 0.020 and 0.024 Å relative to the corresponding monosubstituted ethylenes ( $r_{\text{C-O}} = 1.376$  Å,  $r_{\text{C-B}} = 1.549$  Å, respectively) due to the contribution of the resonance structures shown in Chart V. Additionally,  $\sigma$ -donors like BeH provide substantial stabilization via strong charge alternation in the X-C-C-O skeleton.

Bouma and Radom<sup>4c</sup> have also examined in detail the influence of  $\text{C}_{(2)}$ -substituted vinyl alcohols. However, they considered only the most stable isomer which is in all cases except for  $\text{BH}_2$ (planar) the cis-isomer. The calculated stabilization energies reported do not follow a clear trend with respect to the electronic property of the substituent. This is due to additional stabilizing contributions from hydrogen bonding between the syn-OH group and the substituent X. In the trans-structures considered here such effects are not operative.

The relative stabilizations found for the  $\text{C}_{(1)}$ -substituted acetaldehydes (reaction 5) are very similar to those obtained for the formyl system (reaction 4). From Table II it can be seen that the energy gain follows not only the same order but is also of comparable magnitude indicating that the influence of the additional  $\text{CH}_3$  group is roughly constant. Turning from the formyl to the acetyl series, the Mulliken populations indicate a remarkable decrease of  $\sigma$ -electron density of about 0.20 e at the carbonyl carbon irrespective of the electronic property of the substituent X. The  $\sigma$ -populations on oxygen and X are almost unaffected. Additionally, no significant changes are found for the  $\pi$ -population in the O-C-X moiety. Thus, despite the chemical intuition and results reported for other parent systems,<sup>26</sup> in the carbonyl series  $\text{CH}_3$  appears to act as a weak  $\sigma$ -acceptor (relative to H) exerting no significant  $\pi$ -interactions. This  $\sigma$ -acceptor capability of  $\text{CH}_3$  has already briefly been mentioned in a theoretical study by Del Bene et al.<sup>4b</sup> on mono- and disubstituted neutral formaldehydes by using a STO-3G basis set. This effect is basis set independent as we have checked it for STO-3G, 3-21G, and 6-31G\* wave functions.<sup>27</sup> In general, stabilization of the neutral keto form arises from both  $\pi$ -donation, which increases the polarization of

(24) Schleyer, P. v. R.; Kos, A. J. *Tetrahedron* **1983**, *39*, 1141.(25) Frenking, G.; Koch, W.; Schaale, M. *J. Comput. Chem.* **1985**, *6*, 189.(26) (a) Hinde, A. L.; Pross, A.; Radom, L. *J. Comput. Chem.* **1980**, *1*, 118. (b) Kemister, G.; Pross, A.; Radom, L. *Ibid.* **1981**, *2*, 470.

(27) A compilation of the Mulliken data calculated by using STO-3G, 3-21G, and 6-31G\* basis sets is available upon request.

**Table IV.** Calculated (HF/6-31G\*///3-21G) and (in Parentheses) Experimental Energy Differences of C<sub>(1)</sub>-Substituted Neutral and Cationic Keto/Enol Pairs

$$\text{CH}_3-\text{C}(\text{O})=\text{X} \rightleftharpoons \text{CH}_2=\text{C}(\text{OH})-\text{X}$$

X	neutral <sup>a</sup>	cations <sup>a</sup>
F	31.5	-14.0
OH(anti)	35.6	-11.4 (-22) <sup>c</sup>
NH <sub>2</sub> (planar)	33.3	-21.0
NH <sub>2</sub> (perpend)	16.1	<i>d</i>
CH <sub>3</sub>	16.8 (11.7) <sup>b</sup>	-4.8 (-14) <sup>c</sup>
BH <sub>2</sub> (planar)	5.4	-5.1
BH <sub>2</sub> (perpend)	17.3	-0.4
BeH	22.3	4.6
H	16.2 (13.9) <sup>b</sup>	-7.9 (12.5) <sup>b</sup>

<sup>a</sup>Energy differences  $\Delta E_{(\text{enol-keto})}$  are given in kcal/mol. Positive values indicate that the keto form is more stable. <sup>b</sup>Reference 2e. <sup>c</sup>Reference 2c. <sup>d</sup>The keto form has been ionized from the nitrogen lone pair. See text.

**Table V.** Theoretical (HF/6-31G\*///3-21G) and (in Parentheses) Experimental Heats of Reaction,  $\Delta H_r^\circ$ , for the Isodesmic Reactions 1<sup>+</sup>-5<sup>+</sup>

substituent X	1 <sup>+</sup>	2 <sup>+</sup>	3 <sup>+</sup>	4 <sup>+</sup>	5 <sup>+</sup>
F	6.4 (11.0) <sup>a</sup>	8.2	-2.6	-1.8 (1.0) <sup>e</sup>	2.1
OH	33.3 (43.0) <sup>b</sup>	33.5	20.2	30.2 (17.7) <sup>e</sup>	30.1
NH <sub>2</sub> (planar)	60.8 (49.8) <sup>c</sup>	48.1	39.6	51.6 (45.8) <sup>e</sup>	35.0
NH <sub>2</sub> (perpend)	11.2 <sup>d</sup>	9.0	1.3 <sup>d</sup>	1.5	-12.1 <sup>d</sup>
CH <sub>3</sub>	16.4 (25.7) <sup>e</sup>	16.5	11.1	23.6 (23.7) <sup>e</sup>	19.6
BH <sub>2</sub> (planar)	3.9	3.7	7.2	11.9	6.5
BH <sub>2</sub> (perpend)	9.7	6.8	6.2	18.8	15.1
BeH	12.4	9.4	11.3	24.9	21.9

<sup>a</sup>Benson, S. W.; Rodgers, A. S.; Walsh, R. *Chem. Rev.* **1969**, *69*, 279. <sup>b</sup>Estimated by using ref 31 and 33. <sup>c</sup>Estimated by taking experimental  $\Delta H_r^\circ$  (ethylene imine<sup>+</sup>) from ref 31, the calculated energy difference ethylene imine<sup>+</sup>/vinyl amine<sup>+</sup> (-30.4 kcal/mol; HF/6-31G\*///3-21G) and  $E_{\text{ad}}$  from ref 34. <sup>d</sup>Ionization from the nitrogen lone pair. See text. <sup>e</sup>Reference 33. <sup>f</sup>Calculated total energies (HF/6-31G\*///3-21G) of the species used for the reference system (in hartrees): CH<sub>4</sub>, -40.19517; CH<sub>3</sub>F, -139.03333; CH<sub>3</sub>OH, -115.03376; CH<sub>3</sub>NH<sub>2</sub>, -95.20983; CH<sub>3</sub>CH<sub>3</sub>, -79.22861; CH<sub>3</sub>BH<sub>2</sub>, -65.44153; CH<sub>3</sub>BeH -54.81593. Energies are given in kcal/mol.

the C-O bond by resonance, and  $\sigma$ -acceptance, which diminishes the charge on the carbonyl C-atom thus leading to strong charge alternation in the  $\sigma$ -framework. Thus, the relative stabilities of neutral keto/enol pairs of substituted vinyl alcohol vs. the corresponding acetaldehyde derivatives can be described by the very same effects outlined above, build on top of the basic energy difference between acetaldehyde and vinyl alcohol which is 16.2 kcal/mol (HF/6-31G\*///3-21G). In Table IV the calculated energy differences  $\Delta E = E_{\text{keto form}} - E_{\text{enol form}}$  are listed together with experimentally derived data.

It is evident that for C<sub>(1)</sub>-substituted tautomeric pairs the energy difference has drastically changed for acetyl fluoride, acetic acid, and acetamide. According to the isodesmic reactions 2 and 5, this is due to a much more efficient stabilization of the keto

tautomer by both  $\pi$ -donation and  $\sigma$ -acceptance. These electronic properties reinforce polarization and charge alternation in the molecule which is more powerful in the initially stronger polarized keto form. It is noteworthy to mention the special effects exerted by BH<sub>2</sub> substituents. From Table I it can be seen that acetyl borane prefers a perpendicular arrangement of the BH<sub>2</sub> group. A  $\pi$ -acceptor like BH<sub>2</sub>(planar) destabilizes the keto form. Thus, a decrease or even a reversal of the stability order of neutral keto/enol pairs should be expected for substituents which are very strong  $\pi$ -acceptors, e.g., CN, NO<sub>2</sub>, and CHO. Experimental confirmation for this interpretation is reported in an earlier study of Dubois et al.<sup>1h</sup> They measured the equilibrium constants for the enolization of ring-substituted acetophenones. With increasing  $\pi$ -acceptor capability an increase of enolization is found. Similar conclusions were drawn in a theoretical study by Bouma and Radom<sup>4c</sup> for the keto/enol energy differences of neutral C<sub>(2)</sub>-substituted acetaldehyde/vinyl alcohol derivatives. Again, keto destabilization as well as enol stabilization are achieved by substituents which are both  $\pi$ - and  $\sigma$ -acceptors.

**2. Cationic Systems. A. Substituent Effects on C=C and C=O Double Bond Containing Molecules.** As for any electron deficient system, stabilization is expected to be the higher the more effective the positive charge can be delocalized. Consequently, the direction of the electronic effect is expected to play an important role. As the results of the isodesmic reactions 1<sup>+</sup> (Table V) indicate, a dramatic increase in stabilization of ionized ethylene arises from either  $\pi$ -donating substituents like NH<sub>2</sub> and OH or  $\sigma$ -donating groups. Obviously, the donor ability of the substituent, be it  $\sigma$  or  $\pi$ , is the dominant factor. This is demonstrated by the maximum stabilization of 60.8 kcal/mol found for NH<sub>2</sub>(planar) and the increase of stabilization following the order BH<sub>2</sub>(planar) < BH<sub>2</sub>(perpendicular) < BeH. Electron acceptance is counter-effective and strong electron-withdrawing substituents like F and BH<sub>2</sub>(planar) are stabilizing less efficiently. The large difference in the total energies of species 1<sup>+</sup> with X = NH<sub>2</sub>(planar) and X = NH<sub>2</sub>(perpendicular) of 49.6 kcal/mol favoring the planar structure reveals the importance of  $\pi$ -donation the planar structure reveals the importance of  $\pi$ -donation and is directly attributed to the  $\pi_{\text{C-N}}$ -bond strength.  $\pi$ -Donation by NH<sub>2</sub>(planar) into the C-C bond (see Table VI) turns out to be substantially larger (0.53 e) than in the corresponding neutral system (0.12 e, see Table III). Consequently, the C-N bond is shortened from 1.378 Å in the neutral species to 1.303 Å in the cation.

$\pi$ -Acceptance is destabilizing. BH<sub>2</sub>(planar) stabilizes only by 3.9 kcal/mol, and stronger  $\pi$ -acceptors are expected to destabilize ionized ethylenes. As a consequence, in the cationic vinyl borane the perpendicular arrangement of the BH<sub>2</sub> group is predicted to be more stable than the planar conformation by approximately 5.8 kcal/mol. Furthermore, the comparison of neutral and ionized CH<sub>2</sub>=CHBH<sub>2</sub> reveals that the  $\pi$ -electron withdrawal by BH<sub>2</sub>(planar) is much stronger in the neutral system (-0.18 e) than in the cation radical (-0.03 e). This is reflected by the C-B bond in cationic vinyl borane (1.634 Å) being 0.085 Å longer compared to the neutral species (1.549 Å). In summary, substituted ethylene cation radicals are significantly stabilized by electron-donating groups irrespective of whether they are  $\sigma$ - or  $\pi$ -donors; despite the fact that the cation radicals 1<sup>+</sup> are of <sup>2</sup>A'' symmetry,  $\sigma$ -donors like BeH (and Li)<sup>28</sup> exert significant stabilization by charge

**Table VI.**  $\pi$ - and  $\sigma$ -Charge Transfer from the Substituent X into the Double Bond (Cationic Species)

X	1 <sup>+</sup>		2 <sup>+</sup>		3 <sup>+</sup>		4 <sup>+</sup>		5 <sup>+</sup>	
	$\pi$	$\sigma$	$\pi$	$\sigma$	$\pi$	$\sigma$	$\pi$	$\sigma$	$\pi$	$\sigma$
F	+0.13	-0.34	+0.10	-0.32	+0.10	-0.36	+0.14	-0.28	+0.13	-0.32
OH	+0.29	-0.28	+0.22	-0.26	+0.23	-0.29	+0.25	-0.21	+0.21	-0.22
NH <sub>2</sub> (planar)	+0.53	-0.26	+0.38	-0.23	+0.48	-0.27	+0.40	-0.20	+0.39	-0.17
NH <sub>2</sub> (perpend)	+0.86 <sup>a</sup>	-0.29 <sup>a</sup>	+0.04	-0.03	+0.96 <sup>a</sup>	-0.41 <sup>a</sup>	-0.11	+0.65	-0.03 <sup>a</sup>	+0.61 <sup>a</sup>
CH <sub>3</sub>	+0.05	+0.18	+0.05	+0.19	+0.05	+0.11	+0.07	+0.22	+0.06	+0.23
BH <sub>2</sub> (planar)	-0.03	+0.42	-0.01	+0.39	-0.02	+0.31	0.00	+0.51	-0.02	+0.44
BH <sub>2</sub> (perpend)	-0.03	+0.44	+0.03	+0.37	+0.03	+0.34	+0.04	+0.43	+0.02	+0.40
BeH	+0.50 <sup>b</sup>	0.00	-0.01	+0.47	-0.03	+0.46	+0.03 <sup>c</sup>	+0.77	-0.02	+0.56
H		+0.33		+0.34		+0.34		+0.38		+0.38

<sup>a</sup> Ionization from the nitrogen lone pair. See text. <sup>b</sup> Complex between the ethenyl radical and BeH<sup>+</sup>. See text.

transfer resulting in an electrostatically bound complex between the vinyl radical and  $\text{BeH}^+$  (or  $\text{Li}^+$ ). The C-C bond in  $\text{H}_2\text{C}=\text{CHBeH}^+$  is shortened to 1.371 Å being in between that found in the ethylene radical cation (1.403 Å) and the ethenyl radical (1.329 Å). In contrast, electron-withdrawing groups produce much smaller stabilization or are even destabilizing. These findings are in line with earlier investigations by Apeloig, Schleyer, and Pople<sup>29</sup> on the stability of substituted carbenium ions. The data for the isodesmic reaction 4<sup>+</sup> (Scheme I, Table V) show for ionized formaldehyde derivatives nearly the same order of stabilization as found for the ionized ethylene in reaction 1<sup>+</sup>. Again, electron-donating groups are stabilizing. Moreover, the comparison indicates that the strongly polarized C-O system is more sensitive to inductive electron withdrawal and donation than the corresponding C-C system. Stronger electronegative substituents like F, OH,  $\text{NH}_2$  stabilize less efficiently (or even destabilize in the case of F) while strong electropositive groups stabilize more efficiently compared to reaction 1<sup>+</sup>. Following the Mulliken population, all atoms of unsubstituted formaldehyde radical cation carry positive charges. This very unfavorable situation is removed by  $\pi$ -donating substituents resulting in reinforced charge alternation in the  $\pi$ -framework. The cation radicals 4<sup>+</sup> are of  $^2A'$  symmetry, and the single occupied MO is a nonbonding  $a'$  orbital on oxygen. Thus, the electron deficiency in the  $\sigma$ -framework induces a strong  $\pi$ -transfer into the carbonyl group. Consequently, the  $\pi$ -transfer from X in ionized formamide (+0.40 e) is stronger than in the corresponding neutral species (+0.17 e). The C-O bonds in ionized formic acid and formamide compared to ionized formaldehyde are elongated by 0.052 and 0.086 Å, respectively, according to the resonance structures shown in Chart III. Thus, stabilization by  $\text{NH}_2$  and OH follows the order of their  $\pi$ -donor abilities or, equivalently, their  $\pi$ -polarizabilities. The destabilizing effect of  $\pi$ -electron-withdrawing groups is clearly indicated by comparing the two conformers of  $\text{HCOBH}_2^{2+}$ . The perpendicular form turns out to be more stable by 6.9 kcal/mol than the planar structure due to hyperconjugation between the  $\pi_{\text{BH}_2}$  and the  $p_y(\text{C})$ -orbital. The gain in energy provided by strong electropositive substituents like BeH in the carbonyl system is even more pronounced than for the ethylene cation radical analogues (24.9 kcal/mol vs. 12.4 kcal/mol, respectively). BeH provides stabilization via its tendency to carry most of the positive charge to form an electrostatically bound complex between the formyl radical and  $\text{BeH}^+$ .  $\sigma$ -Donation reduces the positive charge on oxygen from +0.64 in ionized formaldehyde to +0.41. The  $\sigma$ -charge on carbon even turns from +0.44 to -0.55. Thus, the  $\sigma$ -framework is polarized toward the carbon atom whereas a reverse polarization is found for the  $\pi$ -framework. This double polarization results in the shortest C-O bond (1.224 Å) found in this series. The relative stabilization of BeH-substituted cationic ethylene and formaldehyde is mainly determined by the energy difference between the respective neutral species, i.e., the vinyl and the formyl radical.

In a very recent paper, Cremer et al.<sup>30</sup> have investigated substituent effects on the stereomutation mechanism of protonated formaldehyde derivatives. In a similar isodesmic comparison (X = F, OH,  $\text{NH}_2$ , and  $\text{CH}_3$ ) they have obtained stabilization energies which are numerically very close to the results from our cation radical systems (reactions 4<sup>+</sup>). Moreover, they found a very large destabilization for X =  $\text{NO}_2$  which should also apply for the respective cation radical.

**B. Substituent Effects on Cationic Keto/Enol Pairs.** Contrary to neutral vinyl alcohol for which the syn-conformer represents the most stable conformer, the cation radical prefers an anti-conformation.<sup>2e,3a-d,31</sup> We find a difference of 2.0 kcal/mol

favoring the anti-conformation (HF/6-31G\*//3-21G). However, this stability order is dependent upon the bulkiness of the substituent adjacent to  $\text{C}_{(1)}$ .<sup>10</sup> In order to circumvent effects due to repulsions between the hydroxy hydrogen atom and the hydrogen periphery of the substituent, we have considered the ionic syn-conformer throughout in the isodesmic reactions 2<sup>+</sup> and 3<sup>+</sup>. The data for reaction 2<sup>+</sup> (Scheme I, Table V) show the same trend as found for reaction 1<sup>+</sup>: electron donation, again, is the most important factor to provide a substantial gain in stabilization of the vinyl alcohol cation radical. This holds for both  $\text{C}_{(1)}$ - and  $\text{C}_{(2)}$ -substituted isomers (reactions 2<sup>+</sup> and 3<sup>+</sup>). However,  $\text{C}_{(2)}$ -substituted species are by 5–10 kcal/mol less stabilized by F, OH, and  $\text{NH}_2(\text{planar})$  than their corresponding  $\text{C}_{(1)}$ -substituted isomers. This is a consequence of the loss of stabilizing Coulomb attraction by charge alternation in the C-C moiety.<sup>32</sup> The differences in stabilization by F, OH, and  $\text{NH}_2(\text{planar})$  between  $\text{C}_{(1)}$ - and  $\text{C}_{(2)}$ -substituted neutral species have been retained in the charged systems. Thus, the arguments outlined for explaining the stability order of the geminal and trans-vicinal-functionalized neutral vinyl alcohol should also apply for the cationic species, i.e., efficient stabilization of the  $\text{C}_{(1)}$ -substituted cation by polarization of both the  $\sigma$ - and  $\pi$ -framework, respectively. This is in line with theoretical findings concerning the stability order of neutral and charged difluoroethylenes, published recently.<sup>25</sup> For the  $\text{C}_{(1)}$ -substituted vinyl alcohol cation radical  $\text{BH}_2(\text{planar})$  stabilizes less efficiently than  $\text{BH}_2(\text{perpendicular})$  because of its  $\pi$ -withdrawal from an already electron deficient  $\pi$ -system. In contrast,  $\text{C}_{(2)}$ -substituted cationic vinyl alcohol is slightly more stabilized by  $\text{BH}_2(\text{planar})$  as a consequence of a "push-pull" effect.

The stabilization energies found for the cationic formyl system (reaction 4<sup>+</sup>) are very similar to those obtained for the  $\text{C}_{(1)}$ -substituted cationic acetaldehyde derivatives (reaction 5<sup>+</sup>). Thus, it can be concluded that the methyl group exerts a marginal effect on the electronic situation in the O-C-X moiety of the cation radical in question. As in the neutral system,  $\text{CH}_3$  turns out to act as a weak  $\sigma$ -acceptor with insignificant  $\pi$ -interactions. Again, a constant electron withdrawing from the carbonyl carbon by roughly 0.20 e is found irrespective of the electronic nature of the substituent X.

Consequently, the same arguments presented in the discussion of ionized formaldehyde derivatives apply for these species. A general comment seems in order. The isodesmic comparisons involving cationic open-shell species can give rise to useful descriptions of substituent effects only if ionization has taken place at the same structural unit of the molecule in both the substituted as well as the reference system, respectively. This was true for all processes discussed above except for some species with perpendicular arrangement of  $\text{NH}_2$ . Here, the spin density indicates that ionization has taken place from the high-lying nitrogen lone pair whereas the reference system acetaldehyde has been ionized from the C-C-O moiety. Consequently, these species have been omitted from consideration. As mentioned at the beginning of the paper, the cationic enol forms in most cases turn out to be more stable than their tautomeric keto counterparts. Ionized vinyl alcohol is by 7.9 kcal/mol (HF/6-31G\*//3-21G, exptl 12.5 kcal/mol<sup>12e</sup>) more stable than the acetaldehyde cation radical (see Table VI), and this keto/enol energy difference is extremely sensitive to substituents. Ionized acetamide is by 21.0 kcal/mol (HF/6-31G\*//3-21G) less stable than its corresponding enol tautomer.  $\sigma$ -Releasing and  $\pi$ -withdrawing substituents like  $\text{BH}_2(\text{planar})$  diminish the keto/enol energy gap (5.1 kcal/mol) or, for BeH (-4.6 kcal/mol), even revert the order of relative stabilities of ionic keto/enol pairs. Cationic keto/enol pairs

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(32) For a discussion of geometries, charges, and spin densities in 1,1- and 1,2-dihydroxyethylene cation radicals, see: Kalcher, J.; Olbrich, G. *J. Mol. Struct.* **1983**, *104*, 341.

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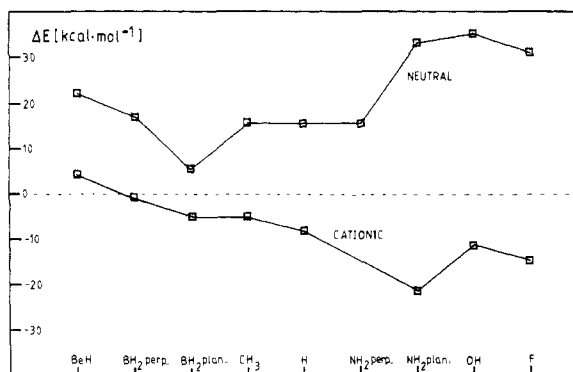
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(28) Lithium shows the strongest stabilization by 74.4 kcal/mol (HF/6-31G\*//3-21G). The lithium atom is highly positively charged by +0.84, and the C-Li bond length amounts to 2.306 Å being 0.325 Å longer than in the neutral species.

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(30) (a) Cremer, D.; Gauss, J.; Childs, R. F.; Blackburn, C. *J. Am. Chem. Soc.* **1985**, *107*, 2435. (b) Blackburn, C.; Childs, R. F.; Cremer, D.; Gauss, J. *Ibid.* **1985**, *107*, 2442.



**Figure 1.** Calculated (HF/6-31G\*\*//3-21G) energy differences of neutral and cationic keto/enol pairs.

containing very electropositive substituents can be described as electrostatically bound complexes between the double bond containing moiety and the positively charged substituent.

### Conclusions

The following conclusions can be drawn from our theoretical study: (1) Neutral ethylenes are thermochemically stabilized by strong  $\pi$ -interacting substituents irrespective of whether they are  $\pi$ -donors or  $\pi$ -acceptors. Stabilization also arises from strongly  $\sigma$ -accepting substituents leading to substantial charge alternation in the molecular skeleton. (2) Formaldehyde derivatives are stabilized by those groups which reinforce the polarization in the C–O bond either by  $\pi$ -donation or  $\sigma$ -acceptance. The magnitude of energy gain of the C=O double bond containing species is larger compared to the C=C double bond containing analogues due to the strong polarization of the multiple bond in the parent H<sub>2</sub>C=O system. (3) In neutral vinyl alcohol, geminal substitution by  $\pi$ -donating and  $\sigma$ -accepting groups is more stabilizing than vicinal substitution. Vicinal substitution is only stabilizing in the case of  $\pi$ -accepting substituents due to a “push-pull” effect. (4)  $\sigma$ -Acceptors and  $\pi$ -donors provide substantial stabilization in C<sub>(1)</sub>-substituted acetaldehydes. (5) The energy difference of neutral C<sub>(1)</sub>-functionalized keto/enol pairs is enlarged for  $\pi$ -donors due to the more efficient stabilization of the keto form which is always the more stable isomer. For  $\pi$ -acceptors, the enol form

is better stabilized, and, consequently, the energy gap decreases. Strong electropositive substituents, again, increase the energy difference due to increased stabilization of the keto tautomer. (6) Ionic ethylene is efficiently stabilized by donating groups irrespective of whether they are  $\sigma$ - or  $\pi$ -donors. (7) The same order of stabilization as in ionic ethylene was found for cationic formaldehyde derivatives. The magnitude of energy gain by  $\pi$ -donors is somewhat lower than in the cationic ethylenes whereas electropositive  $\sigma$ -donating groups are stabilizing more efficiently. (8) Stabilization of cationic C<sub>(1)</sub>-substituted acetaldehyde is very similar to that of the corresponding formaldehyde derivatives. (9) Because of more efficient stabilization of ionized vinyl alcohol by  $\pi$ -donating groups, the keto/enol energy gap (favoring the enol form) is increased. With increasing  $\sigma$ -donor ability the stabilization of the keto isomer becomes more efficient exceeding that for the enol tautomer. (10) Regarding the relative stabilization of neutral and ionic keto and enol tautomers and the corresponding energy differences (graphically summarized in Figure 1), the following prediction can be made: very strong  $\pi$ -accepting C<sub>(1)</sub>-substituents like NO<sub>2</sub> or CHO should stabilize the neutral enol form and destabilize the keto form remarkably, thus leading to a relatively small keto/enol energy gap or even to a reversal of the stability order. In the ionic cases a reversal of the usually observed stability order is predicted for the BeH-substituted system. This effect should be larger the more electropositive and  $\sigma$ -donating the substituent acts, e.g., MgBr.

**Acknowledgment.** We are indebted to Professors Y. Apeloig and Z. Rappoport for stimulating remarks and to Prof. P. v. R. Schleyer and his group for making available to us the modified version of the GAUSSIAN 76 program. The continuous support of our work by the Fonds der Chemischen Industrie, the Deutsche Forschungsgemeinschaft (Projekt Schw 221/7-2), and the Gesellschaft von Freunden der Technischen Universität is gratefully acknowledged. We are particularly indebted to the Computer Center of TUB and the Konrad-Zuse-Zentrum für Informationstechnik Berlin for generously providing computer time.

**Supplementary Material Available:** Tables SI–SX containing bond lengths, atomic total charges, and  $p_y$ -(out-of-plane)-orbital populations for structures 1–5 and 1<sup>+</sup>–5<sup>+</sup> (10 pages). Ordering information is given on any current masthead page.