J. Am. Chem. Soc. **2001,** *123,* 2430−2431

Ab Initio Study of the Carbon-to-Carbon Identity Proton Transfer from Ketene to Its Anion in the Gas Phase

Claude F. Bernasconi* and Philip J. Wenzel

Department of Chemistry and Biochemistry
University of California, Santa Cruz, California 95064

Received November 2, 2000
Revised Manuscript Received December 18, 2000

There is continued and accelerating interest in the factors that determine the Marcus intrinsic barriers and transition state structures (henceforth TS) of proton-transfer reactions.[1] Here we report the intrinsic barrier of the identity carbon-to-carbon proton transfer shown in eq 1 as calculated by ab initio methods. We

$$O{=}C{=}CH_2 + HC{\equiv}C{-}O^- \rightleftharpoons {}^-O{-}C{\equiv}H + CH_2{=}C{=}O \tag{1}$$

also address the question of how the higher degree of unsaturation in ketene compared to acetaldehyde may affect the TS imbalance[4] typical for such reactions.[5]

Additional motivation for this study was provided by results regarding the rate of protonation of ynolate ions such as $PhC{\equiv}CO^-$ by H^+ in aqueous solution.[6] The k_{H^+} value of 1.34×10^{10} M^{-1} s^{-1} is close to the diffusion-controlled limit and much higher than k_{H^+} for the corresponding enolate ion, $PhCH{=}CHO^-$ (1.6×10^7 M^{-1} s^{-1}).[7]

The higher k_{H^+} value for the ynolate ion could be the result of either a higher pK_a or a lower intrinsic barrier. Based on gas-phase acidities of ketene and acetaldehyde,[8] it is unlikely that $PhC{\equiv}CO^-$ is more basic than $PhCH{=}CO^-$, making the second explanation more plausible. Our results support this conclusion.

We report calculations at the MP2/6-311+G(d,p)//MP2/6-311+G(d,p) (MP2//MP2) and B3LYP/6-311+G(d,p) levels; gas-phase acidities were also recomputed at the CCSD(T)/6-311+G-(2df,2p) level. For details see the Supporting Information.[9]

Acidities. Our acidities (Table 1) are higher than the ones reported by Smith et al.[10] (369.6 kcal/mol at MP4/6-311+G(d,p)) but in good agreement with experiment;[8] at all levels, except for B3LYP/6-311+G(d,p) ketene is slightly more acidic than acetaldehyde.

Table 1. Gas-Phase Acidities ($\Delta H°$) and Intrinsic Barriers of Identity Proton Transfers ($\Delta H^{\ddagger}$)[a]

	MP2/6-311+ G(d,p)// MP2/6-311+ G(d,p)	B3LYP/ 6-311+ G(d,p)	CCSD(T)/ 6-311+ G(2df,2p)	exptl[b]
	$\Delta H°$ (kcal/mol)			
$CH_2{=}C{=}O$	364.4	364.0	366.1	364.9 ± 2.6
$CH_3CH{=}O^c$	367.2	363.5	367.3	365.8 ± 2.9
$CH_2{=}CH_2$	407.9	406.3	408.4	406.0 ± 2.0
CH_3CH_3	420.2	418.4	420.2	421.0 ± 2.0
CH_4 [c]	418.1	415.3	418.0	416.6 ± 0.8
	$\Delta H^{\ddagger}$ (kcal/mol)			
$CH_2{=}C{=}O$	$-7.8\ (-4.2)^d$	$-8.9\ (-8.4)^d$		
$CH_3CH{=}O^c$	$-0.3\ (2.7)^d$	$-1.8\ (-1.3)^d$		
$CH_2{=}CH_2$	$3.9\ (7.0)^d$	$3.4\ (4.2)^d$		
CH_3CH_3	$4.8\ (9.3)^d$	$6.0\ (7.7)^d$		
CH_4 [c]	$8.1\ (12.1)^d$	$6.7\ (7.9)^d$		

[a] $\Delta H^{\ddagger} = H^{\ddagger} - H$(reactants). [b] Reference 8. [c] Reference 3i. [d] Numbers in parentheses are corrected for BSSE (see text).

As shown recently,[3i] the dominant factor enhancing the acidity of acetaldehyde relative to methane or ethane (Table 1) is resonance stabilization of the enolate ion, worth ca. 36.6 kcal/mol relative to methane, while the field effect of the $CH{=}O$ group contributes about 13.3 kcal/mol. The greater acidity of ketene compared to ethene is undoubtedly the result of a similar combination of resonance and field effects of the $C{=}O$ group. The importance of the resonance effect is apparent from the geometric parameters (Table 2) and the group charges (Table 3). The conversion of ketene to its anion is associated with a significant $C{=}C$ bond contraction/$C{=}O$ bond elongation and an opening of the HCC bond angle from 119° to 142°, consistent with a significant contribution of **1b** to the resonance hybrid. This

$$\underset{\textbf{1a}}{H\bar{C}{=}C{=}O} \leftrightarrow \underset{\textbf{1b}}{HC{\equiv}C{-}O^-}$$

is similar to the corresponding bond changes for acetaldehyde versus its enolate ion.[11] The accumulation of negative charge on the $C{=}O$ group in the anion (Table 3) further supports the importance of **1b**.

The fact that the acidity difference between ketene and acetaldehyde is much smaller than that between ethene and ethane implies that the ynolate ion stabilizing effect of $C{=}O$ is smaller than the enolate ion stabilizing effect of $CH{=}O$. The greater ability of the sp^2 carbon in ketene compared to the sp^3 carbon in acetaldehyde to support the charge apparently reduces the dependence on the substituent. The increased s-character is, of course, also the main reason ethene is more acidic than ethane.

Transition State Structure. The changes in geometry and group charges in moving to the TS for the ketene are quite similar to those for the corresponding acetaldehyde reaction (eq 2).[11] The

$$O{=}CH{-}CH_3 + CH_2{=}CH{-}O^- \rightleftharpoons {}^-O{-}CH{=}CH_2 + CH_3{-}CH{=}O \tag{2}$$

largest difference is in the progress of angle deformation (47.1%

---

(1) The literature on proton transfers is extensive. Only a few of the most recent references are listed here.[2,3]

(2) Solution reactions: (a) Nevy, J. B.; Hawkinson, D. C.; Blotny, G.; Yao, X.; Pollack, R. M. *J. Am. Chem. Soc.* **1997**, *119*, 12722. (b) Moutier, G.; Peigneux, A.; Vichard, D.; Terrier, F. *Organometallics* **1998**, *17*, 4469. (c) Bernasconi, C. F.; Kittredge, K. W. *J. Org. Chem.* **1998**, *63*, 1944. (d) Richard, J. P.; William, G.; Gao, J. *J. Am. Chem. Soc.* **1999**, *121*, 715. (e) Bernasconi, C. F.; Moreira, J. H.; Huang, L. L.; Kittredge, K. W. *J. Am. Chem. Soc.* **1999**, *121*, 1674. (f) Terrier, F.; Moutiers, G.; Pelet, S.; Buncel, E. *Eur. J. Org. Chem.* **1999**, 1771.

(3) Theoretical studies: (a) Bernasconi, C. F.; Wenzel, P. J.; Keeffe, J. R.; Gronert, S. *J. Am. Chem. Soc.* **1997**, *119*, 4008. (b) Agback, M.; Lunell, S.; Hussénius, A.; Matsson, O. *Acta Chem. Scand.* **1998**, *52*, 541. (c) Bekšic, D.; Bertrán, J.; Lluch, J. M.; Hynes, J. T. *J. Phys. Chem. A* **1998**, *102*, 3977. (d) Harris, N.; Wei, W.; Saunders, W. H., Jr.; Shaik, S. S. *J. Phys. Org. Chem.* **1999**, *12*, 259. (e) Van Verth, J. E.; Saunders, W. H., Jr. *Can. J. Chem.* **1999**, *77*, 810. (f) Yamataka, H.; Mustamir; Mishima, M. *J. Am. Chem. Soc.* **1999**, *121*, 1023. (g) Lee, I.; Kim, C. K. *J. Phys. Org. Chem.* **1999**, *12*, 255. (h) Harris, N.; Wei, W.; Saunders, W. H., Jr.; Shaik, S. S. *J. Am. Chem. Soc.* **2000**, *122*, 6754. (i) Bernasconi, C. F.; Wenzel, P. J. *J. Org. Chem.* **2001**, *66*, 968.

(4) The imbalance refers to the fact that charge delocalization into the π-acceptor lags behind the proton transfer at the transition state.

(5) (a) Bernasconi, C. F. *Acc. Chem. Res.* **1987**, *20*, 301. (b) Bernasconi, C. F. *Adv. Phys. Org. Chem.* **1992**, *27*, 119. (c) Bernasconi, C. F. *Acc. Chem. Res.* **1992**, *25*, 9.

(6) Chiang, Y.; Kresge, A. J.; Popik, V. V. *J. Am. Chem. Soc.* **1995**, *117*, 9165.

(7) Keeffe, J. R.; Kresge, A. J. In *The Chemistry of Enols*; Rappoport, Z., Ed.; Wiley & Sons: New York, 1990; p 399.

(8) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Levin, R. D.; Holmes, J. L.; Mallard, W. G. Gas-Phase Ion and Neutral Thermochemistry. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.

(9) See Supporting Information paragraph at the end of this paper.

(10) Smith, B. J.; Radom, L.; Kresge, A. J. *J. Am. Chem. Soc.* **1989**, *111*, 8297.

(11) (a) Saunders, W. H., Jr. *J. Am. Chem. Soc.* **1994**, *116*, 5400. (b) Bernasconi, C. F.; Wenzel, P. J. *J. Am. Chem. Soc.* **1994**, *116*, 5405. (c) Bernasconi, C. F.; Wenzel, P. J. *J. Am. Chem. Soc.* **1996**, *118*, 10494.

10.1021/ja003858x CCC: $20.00

Table 2. Geometries (MP2//MP2)[a]

parameter	acid	anion	TS	% progress at TS
		$CH_2{=}C{=}O$		
$r_{C=C}$	1.322	1.271	1.293	
$\Delta r_{C=C}$		−0.051	−0.029	56.9
$100\{\lvert\Delta r_{C=C}\rvert/r_{C=C}\}$		3.86		
$r_{C=O}$	1.168	1.229	1.201	
$\Delta r_{C=O}$		0.061	0.033	54.1
$100\{\Delta r_{C=O}/r_{C=O}\}$		5.22		
α_{HCC}	119.1	141.6	129.7	
$\Delta\alpha_{HCC}$		22.5	10.6	47.1
r_{C-H} [b]			1.374	
		$CH_3CH{=}O$[c]		
r_{C-C}	1.503	1.391	1.430	65.2
Δr_{C-C}		−0.112	−0.073	
$100\{\lvert\Delta r_{C-C}\rvert/r_{C-C}\}$		7.45		
$r_{C=O}$	1.215	1.271	1.246	55.4
$\Delta r_{C=O}$		0.056	0.031	
$100\{\Delta r_{C=O}/r_{C=O}\}$		4.60		
α_{pyr}	51.55	0.00	37.32	
$\Delta\alpha_{pyr}$		−51.55	14.23	27.6
r_{C-H} [b]			1.416	
		$CH_2{=}CH_2$		
$r_{C=C}$	1.339	1.365	1.353	
$\Delta r_{C=C}$		0.026	0.014	53.8
r_{C-H} [b]			1.424	
		CH_3CH_3		
r_{C-C}	1.529	1.536	1.530	
Δr_{C-C}		0.007	0.001	
r_{C-H} [b]			1.436	

[a] For geometries at the B3LYP level see Table S1.[9] [b] H refers to the proton in flight. [c] Reference 3i.

Table 3. NPA Group Charges (MP2//MP2)[a]

group	acid	anion	diff[b]	TS	diff[c]	n
			$CH_2{=}C{=}O$			
$CH_2(CH)$	−0.273	−0.660	−0.387	−0.598	−0.325[e]	
$C{=}O$	0.273	−0.340	−0.613[d]	−0.051	−0.324[f]	1.47
H in flight				0.297		
			$CH_3CH{=}O$			
$CH_3(CH_2)$	−0.021	−0.469	−0.448	−0.384	−0.363[e]	
$CH{=}O$	0.021	−0.531	−0.522[d]	−0.266	−0.287[f]	1.52
H in flight				0.301		
			$CH_2{=}CH_2$			
$CH_2(CH)$	0	−0.628	−0.628	−0.400	−0.400[e]	
CH_2	0	−0.372	−0.372[d]	−0.225	−0.225[f]	(1.06)
H in flight				0.249		
			CH_3CH_3			
$CH_3(CH_2)$	0	−0.798	−0.798	−0.530	−0.530[e]	
CH_3	0	−0.202	−0.202[d]	−0.107	−0.107[f]	(0.91)
H in flight				0.273		
CH_4						
H in flight				0.315		

[a] Atomic charges as well as charges at the B3LYP level, including Mulliken charges, are reported in Table S2.[9] [b] Anion-acid. [c] TS-acid. [d] |difference| = χ in eq 3. [e] |difference| = δ_C in eq 3. [f] |difference| = δ_Y in eq 3.

for the HCC angle in the ketene reaction versus 27.6% for the pyramidal angle of the acetaldehyde reaction), suggesting that the lag in charge delocalization behind bond proton transfer (imbalance) is less pronounced in the ketene reactions; note that, due to symmetry, the progress of the proton transfer is 50% in both cases.

Another measure of imbalance is the *n*-parameter[11b,11c] (eq 3), where δ_Y, δ_C, and χ are group charge differences between TS

$$n = \log(\delta_Y/\chi)/\log(\delta_C + \delta_Y) \tag{3}$$

and neutral acid (δ_Y, δ_C), or between the anion and acid (χ), respectively (see footnotes *d*−*f* in Table 3). The *n* value of 1.47 for the ketene reaction compares with $n = 1.52$ for the acetaldehyde reaction, suggesting the ketene TS is slightly less imbalanced than the acetaldehyde TS, consistent with the conclusion based on the angles α_{HCC} and α_{pyr}, respectively.[13]

Barriers. Barriers are reported in Table 1 with and without correction for BSSE by the counterpoise method.[14] In view of the controversy as to whether the counterpoise method may lead to over-correction at the MP2[15] level and the fact that, at a given computational level, the corrections are all very similar for the various reactions, we will focus on the uncorrected values.

(1) The barrier for the ketene reaction is much lower than that for the ethene reaction ($\Delta\Delta H^‡ = 11.7$ kcal/mol at MP2//MP2, 12.3 kcal/mol at B3LYP). This indicates that stabilization of TS by the $C{=}O$ group is greater than stabilization of the ynolate ion. This is mainly because each of the two $CH{=}C{=}O$ fragments carries more than half a negative charge so that the total substituent effect of the two $C{=}O$ groups on the TS is greater than the effect of one $C{=}O$ group on the anion. This situation is analogous to that for eq 2,[3i] which has a lower barrier than the $CH_3CH_3/CH_3CH_2^-$ system ($\Delta\Delta H^‡ = 5.1$ kcal/mol at MP2//MP2, 7.8 kcal/mol at B3LYP).

(2) The barrier for the ketene reaction is significantly lower than that for the acetaldehyde reaction ($\Delta\Delta H^‡ = 7.5$ kcal/mol at MP2//MP2, $\Delta H^‡ = 7.1$ kcal/mol at B3LYP). This result supports the notion that the higher k_{H^+} value for protonation of $PhC{\equiv}CO^-$ compared to the protonation of $PhCH{=}CHO^-$ is the consequence of a lower intrinsic barrier.

(3) A major factor reducing the ketene barrier compared to the acetaldehyde barrier is the greater s-character of the acidic carbon of ketene; it makes the TS tighter ($r_{C-H} = 1.374$ versus 1.416 Å) and also allows more effective stabilization by hydrogen bonding than in the acetaldehyde reaction because an sp^2 carbon is a better hydrogen bond acceptor than an sp^3 carbon.[3a,12] This factor should play a role in any comparison between sp^2 versus sp^3 acids, including ethene versus ethane, although here the difference in $\Delta H^‡$ is much smaller (0.9 kcal/mol at MP2//MP2; 2.6 kcal/mol at B3LYP). The much larger difference between the ketene and acetaldehyde barriers may be the result of the greater negative charge on the CH groups of the ketene TS (−0.598) compared to the charge on the CH_2 groups of the acetaldehyde TS (−0.384); this should increase the hydrogen bonding/electrostatic stabilization of the ketene TS beyond that arising from the strong s-character.

In contrast, the surprisingly small difference in $\Delta H^‡$ between ethene and ethane may arise from the greater negative charges on the CH_2 groups of the ethane TS (−0.530) compared to the charges on the CH groups of the ethene TS (−0.400). The resulting enhanced electrostatic/hydrogen bonding stabilization of the ethane TS could offset some of the inherent advantage of the sp^2 hybridization in the ethene reaction. There appears to be some additional TS stabilization of the ethane reaction by the polarizability effect of the methyl group; this notion is supported by the fact that $\Delta H^‡$ for the $CH_3CH_3/CH_3CH_2^-$ system is lower than that for the CH_4/CH_3^- system.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research (grant PRF 33143-AC4).

Supporting Information Available: Tables S1 (energies), S2 (charges), Figure S1 (geometries) and computational details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA003858X

---

(12) (a) Cybulski, S. M.; Scheiner, S. *J. Am. Chem. Soc.* **1987**, *109*, 4199. (b) Scheiner, S.; Wang, L. *J. Am. Chem. Soc.* **1992**, *114*, 3650. (c) Scheiner, S. *J. Mol. Struct. (THEOCHEM)* **1994**, *307*, 65.

(13) For the ethene and ethane reactions the *n* values are close to unity, implying the absence of a significant imbalance.

(14) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

(15) (a) Cook, D. B.; Sordo, J. A.; Sordo, T. L. *Int. J. Quantum Chem.* **1993**, *48*, 375. (b) Davidson, E. R.; Chakravorty, S. J. *Chem. Phys. Lett.* **1994**, *217*, 48.