

The C–C Bond Is Stronger than the C–Cl Bond in CH₃COCl

E. Arunan[†]

Department of Chemistry, Indian Institute of Technology, Kanpur, India 208 016

Received: February 14, 1997; In Final Form: April 14, 1997[⊗]

The C–C and C–Cl bond dissociation energies, D_0 at 0 K, in CH₃COCl are determined from the recent, accurate experimental enthalpies of formation for CH₃COCl, CH₃, COCl, CH₃CO, and Cl. $D_0(\text{C–C})$ is 85.9 ± 0.8 kcal mol^{−1}, and $D_0(\text{C–Cl})$ is 83.0 ± 1.0 kcal mol^{−1}. This suggests that the C–C bond is stronger than the C–Cl bond in CH₃COCl, unlike what has been assumed in several recent publications on the photodissociation of CH₃COCl. Results from recent *ab initio* calculations agree with this order of bond dissociation energies.

Photodissociation of acetyl chloride has attracted enormous interest recently.^{1–6} It leads to preferential cleavage of the C–Cl bond over that of the C–C bond. In organic photochemistry texts, it has been cited as an example for the Norrish type I photochemical mechanism involving the preferential cleavage of the weaker (C–Cl) bond.⁷ Butler and co-workers recently initiated thorough experimental investigations on the photodissociation of acetyl chloride and related compounds.^{1,2} Their experiments clearly demonstrated the preferential C–Cl bond dissociation on photolysis at 248.5 nm. However, the photofragment angular distribution was highly anisotropic suggesting that the dissociation was impulsive, occurring in a subpicosecond time scale on a singlet excited state. The usual Norrish type I mechanism involves internal conversion to the ground state or intersystem crossing to the lowest triplet state from which the dissociation occurs and the photofragment angular distribution is isotropic.¹ In their original communication,¹ Butler and co-workers estimated the C–Cl bond energy as 83 kcal mol^{−1} from the available experimental enthalpies of formation.⁸ They assumed the C–C bond dissociation energy to be around 80 kcal mol^{−1}, which was the estimated C–C bond energy in acetone.⁹ This assumption had continued in their detailed paper² where it was stated that “C–Cl cleavage should not be cited as an example of fission of the weaker bond, as the C–Cl bond is at least as strong as the C–C bond”.

Hess and co-workers investigated the photodissociation of acetyl chloride by photofragment imaging and have confirmed the anisotropic angular distribution of the Cl photofragment.^{3,4} They also observed CH₃ and CO fragments from secondary dissociation of acetyl radicals, and their angular distribution was isotropic. This observation showed that the primary dissociation involved C–Cl cleavage only. Following ref 1, they noted that “the weaker C–C bond is expected to break preferentially over the stronger C–Cl bond”.³ Very recently they have studied the photodissociation of solid CH₃COCl and identified that the HCl elimination is more important for solid CH₃COCl.⁵ Here again they continued to assert that the C–C bond is weaker than the C–Cl bond. Lee and co-workers⁶ used photofragment translational spectroscopy to study this process and the secondary dissociation of CH₃CO to give CH₃ and CO. They also emphasized that the “dissociation involves exclusive α -cleavage of the stronger C–Cl over the C–C bond”.⁶

Sumathi and Chandra¹⁰ have studied the dissociation dynamics of acetyl chloride by *ab initio* methods following the

experiments by Butler’s group. They optimized the geometries at (U)HF/6-31G* and carried out single-point MP2 calculations for energies. Their results for the bond energies were 81.1 and 87.5 kcal mol^{−1} for C–Cl and C–C respectively, predicting the C–C bond to be stronger than the C–Cl bond. Wiberg et al.¹¹ have, however, estimated the C–Cl bond energy at the same level with the MP2 optimized geometry, and they reported a value of 87.6 kcal mol^{−1}. They did not estimate the C–C bond energy. Interestingly, they have also done single-point calculations at a higher level with the MP2/6-31G* geometry and the C–Cl bond energy at the MP3/6-311++G** level lowered to 76.2 kcal mol^{−1}.

For the ground state CH₃COCl, the 1,2-HCl elimination channel is more important, and its activation barrier was estimated as 48.2 kcal mol^{−1} at the (U)HF/6-31G*// (U)MP2/6-31G* level.¹⁰ We have studied the HX elimination from haloethanes in detail using the infrared chemiluminescence technique.^{12,13} We are currently investigating the unimolecular reaction dynamics of the chemically activated FCH₂COCl*. The FCH₂COCl* could react by several molecular elimination pathways as well as C–C and C–Cl bond dissociation pathways.¹⁴ Accurate estimates of the barrier energies for the different unimolecular reaction pathways were needed to ascertain the importance of the different channels. Again, Sumathi’s calculations on FCH₂COCl at the (U)MP2/6-31G*// (U)MP2/6-31G* level predicted the C–Cl bond (78.4) to be weaker than the C–C bond (82.5).¹⁴ As the accuracy of the MP2/6-31G* bond energies is questionable, we looked for experimental enthalpies of formation for all the radicals involved to corroborate the *ab initio* estimates. Accurate enthalpies of formation are now available for CH₃, COCl, CH₃CO, Cl, and CH₃COCl, which make the calculation of the C–C and C–Cl bond dissociation energy in CH₃COCl straightforward. We estimate the C–C bond energy to be 85.9 ± 0.8 kcal mol^{−1} and the C–Cl bond energy to be 83.0 ± 1.0 kcal mol^{−1}, 2.9 \pm 1.3 kcal mol^{−1} less than the C–C bond energy. The thermochemical data used here are summarized in Table 1 and discussed below.

For CH₃ and Cl radicals, the enthalpies of formation are most certain and the JANAF tables list $\Delta H_f^\circ(0\text{ K})$ as 35.62 ± 0.19 and 28.590 ± 0.002 kcal mol^{−1}, respectively.¹⁵ For COCl, the experimental values now appear to converge. Walker and Prophet had determined the $\Delta H_f^\circ(0\text{ K})$ as -4 ± 3 kcal mol^{−1} in 1967.¹⁶ Wine and co-workers¹⁷ have recently determined the ΔH_f° to be -5.2 ± 0.6 kcal mol^{−1} at 298 K and -5.6 ± 0.7 at 0 K. Atkinson et al.¹⁸ in their compilation have chosen $\Delta H_f^\circ(298\text{ K})$ to be -4.1 (no uncertainty quoted) following

[†] Email: arunan@iitk.ernet.in.

[⊗] Abstract published in *Advance ACS Abstracts*, May 15, 1997.

TABLE 1: Enthalpies of Formation for the Radicals/Molecule

species	$\Delta H_f^\circ(0\text{ K})$	$\Delta H_f^\circ(298\text{ K})$	ref
Cl	28.590 ± 0.002	28.992 ± 0.002	15 ^a
CH ₃	35.62 ± 0.19	34.82 ± 0.19	15 ^a
CH ₃ COCl		-58.0 ± 0.2	22
	-55.9 ± 0.2		11 ^a
COCl	-5.6 ± 0.7	-5.2 ± 0.6	17 ^a
		-4.1	18
	-4 ± 3		16
CH ₃ CO	-1.5 ± 1.0	-3.0 ± 1.0	11 ^a
		-2.4 ± 0.3	23
		-5.4 ± 2.1	24
	-0.55 ± 0.6	-2.2 ± 0.7	20
		-1.8 ± 1.0	21

^a Enthalpies of formation at 0 K used in estimating the C–C and C–Cl bond energies in CH₃COCl. See text for details.

Benson.¹⁹ We prefer the estimate of Wine and co-workers which has a reported uncertainty of only 0.7 kcal mol^{−1} at 0 K. For CH₃CO, the experimental enthalpy of formation at 298 K varies between −2.4 and −10.8 kcal mol^{−1}. Bauschlicher²⁰ has reported high-level calculations (G1 and G2 with an estimated uncertainty of 2 kcal mol^{−1}) on the enthalpy of formation for CH₃CO and has given a summary of experimental data on CH₃CO. He ruled out enthalpy values below −3 kcal mol^{−1} as unrealistic and suggested $\Delta H_f^\circ(\text{CH}_3\text{CO})$ values of -2.2 ± 0.7 at 298 K and -0.55 ± 0.6 at 0 K. Zachariah and co-workers²¹ have reported extensive BAC-MP4 (bond additivity corrected MP4) estimates for some stable and radical hydrofluorocarbons (HFC) and oxidized HFC. Their estimate for $\Delta H_f^\circ(\text{CH}_3\text{CO}, 298\text{ K})$ is $-1.8\text{ kcal mol}^{-1}$. For 70 of these species, their estimates were within 2.2 kcal mol^{−1} of the experimental results. Also, their estimate for $\Delta H_f^\circ(298\text{ K})$ for CH₃ is 34.89 kcal mol^{−1}, nearly identical to the JANAF¹⁵ value at 34.82. Wiberg et al.¹¹ have chosen to use the weighted average of the two recent experimental values (see Table 1), and they suggested ΔH_f° values of -3.0 ± 1.0 at 298 K and -1.5 ± 1.0 at 0 K. Their suggestion is followed here. It should be pointed out that using lower values for $\Delta H_f^\circ(\text{CH}_3\text{CO})$ would lead to an even smaller C–Cl bond dissociation energy in acetyl chloride. For acetyl chloride itself, $\Delta H_f^\circ(298\text{ K})$ is reported²² as $-58.0 \pm 0.2\text{ kcal mol}^{-1}$, which was converted by Wiberg et al.¹¹ to -55.9 ± 0.2 at 0 K.

Using the data given above, the enthalpies for the following reactions are calculated as (enthalpies given in parentheses in kcal mol^{−1} at 0 K):



The error limits quoted are accumulated root mean squares deviations from the error limits reported for the experimental enthalpy data. Instead, if we sum the absolute errors in the enthalpy data, we can obtain an upper bound for errors, and the enthalpies for reactions 1 and 2 are 85.9 ± 1.1 and $83.0 \pm 1.2\text{ kcal mol}^{-1}$, respectively. With the available experimental

data, it is clear that the C–C bond is stronger than the C–Cl bond in CH₃COCl, unlike what has been assumed so far in the literature.^{1–6} However, it must be added that this reversal in the bond strengths does not affect the interpretation of the experiments cited above. In closing, we refer to the excellent review article on bond energies by Berkowitz et al.²⁵ which emphasizes the importance of bond energies.

Acknowledgment. I thank Prof. D. W. Setser who always insisted on using accurate thermochemical data. I thank Prof. N. Sathyamurthy for bringing ref 5 to my attention and for useful discussions. I thank Dr. R. Sumathi for permission to quote results on FCH₂COCl before publication.

References and Notes

- (1) Person, M. D.; Kash, P. W.; Butler, L. J. *J. Phys. Chem.* **1992**, *96*, 2021.
- (2) Person, M. D.; Kash, P. W.; Butler, L. J. *J. Chem. Phys.* **1992**, *97*, 355.
- (3) Deshmukh, S.; Myers, J. D.; Xantheas, S. S.; Hess, W. P. *J. Phys. Chem.* **1994**, *98*, 12535.
- (4) Deshmukh, S.; Hess, W. P. *J. Chem. Phys.* **1994**, *100*, 6429.
- (5) Rowland, B.; Hess, W. P. *Chem. Phys. Lett.* **1996**, *263*, 574.
- (6) North, S.; Blank, D. A.; Lee, Y. T. *Chem. Phys. Lett.* **1994**, *224*, 38.
- (7) Barltrop, J. A.; Coyle, J. D. *Excited States in Organic Chemistry*; Wiley: New York, 1975.
- (8) Devore, J. A.; O'Neal, H. E. *J. Phys. Chem.* **1969**, *73*, 2644.
- (9) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data.*, **1977**, *6* (Suppl. 1), 1-774.
- (10) Sumathi, R.; Chandra A. K. *Chem. Phys.* **1994**, *181*, 73.
- (11) Wiberg, K. B.; Hadad, C. M.; Rablen, P. R.; Cioslowski, J. *J. Am. Chem. Soc.* **1992**, *114*, 8644. Table XII in this paper, which is a useful compilation of enthalpy data, has the enthalpies of formation at 0 and 298 K mixed up for F and Cl.
- (12) Arunan, E.; Wategaonkar, S. J.; Setser, D. W. *J. Phys. Chem.* **1991**, *95*, 1539.
- (13) Arunan, E.; Rengarajan R.; Setser, D. W. *Can. J. Chem.* **1994**, *72*, 568.
- (14) Srivatsava, A. J.; Arunan, E.; Manke, G. II.; Setser, D. W.; Sumathi, R. To be submitted to *J. Phys. Chem.*
- (15) Chase, M. W., Jr.; Davies, C. A.; Downey, J. R., Jr.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data.* **1985**, *14* (Suppl. 1).
- (16) Francisco, J. S.; Goldstein, A. N.; Li, Z.; Zhao, Y.; Williams, I. H. *J. Phys. Chem.* **1990**, *94*, 4791. These authors have quoted the $\Delta H_f^\circ(0\text{ K})$ for COCl from: Walker, L. C.; Prophet, H. *Trans. Faraday Soc.* **1967**, *63*, 879.
- (17) Nicovich, J. M.; Kreutter, K. D.; Wine, P. H. *J. Chem. Phys.* **1990**, *92*, 3539. This paper has a typographical error in the abstract where the enthalpy of formation is listed as $5.2 \pm 0.6\text{ kcal mol}^{-1}$, without the negative sign. Amusingly, this error found its way to the recent work of Schnöckel et al. (*J. Chem. Phys.* **1992**, *97*, 4.) This error, however, did not affect their results or conclusions.
- (18) Atkinson, R.; Baulch, D. L.; Cox, R. A.; Hampson, R. F., Jr.; Kerr, J. A.; Troe, J. *J. Phys. Chem. Ref. Data.* **1989**, *18*, 881.
- (19) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976.
- (20) Bauschlicher, C. W., Jr. *J. Phys. Chem.* **1994**, *98*, 2564.
- (21) Zachariah, M. R.; Westmoreland, P. R.; Burgess, D. R., Jr.; Tsang, W.; Melius, C. F. *J. Phys. Chem.* **1996**, *100*, 8737.
- (22) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: London, 1986.
- (23) Niiranen, J. K.; Gutman, D.; Krasnopetrov, L. N. *J. Phys. Chem.* **1992**, *96*, 5881.
- (24) Nimlos, M. R.; Soderquist, J. A.; Ellison, G. B. *J. Am. Chem. Soc.* **1989**, *111*, 7675.
- (25) Berkowitz, J.; Ellison, G. B.; Gutman, D. *J. Phys. Chem.* **1994**, *98*, 2744.