J. Am. Chem. Soc. **1989**, *111*, 9030-9031

Concerning the Heat of Formation of the Isopropyl Radical

E. Tschuikow-Roux* and Yonghua Chen

Contribution from the Department of Chemistry, University of Calgary,
Calgary, Alberta, Canada T2N 1N4. *Received April 19, 1989*

Abstract: The heat of formation of the isopropyl radical has been reevaluated using the third-law method and kinetic data for the reactions $i\text{-}C_3H_7 \rightleftharpoons C_3H_6 + H$ and $2i\text{-}C_3H_7 \rightleftharpoons$ 2,3-DMB. The result of $\Delta H_f{}^\circ{}_{298}(i\text{-}C_3H_7) = 21.0 \pm 0.5$ kcal mol^{-1} agrees with a recent bromination equilibrium study and is consistent with a small barrier (~ 1 kcal mol^{-1}) for internal rotation for each of the two CH_3 groups as found in an ab initio geometry optimization study.

The importance of accurate heats of formation of simple alkyl radicals in thermochemical kinetics is generally recognized. In particular, the $\Delta H_f{}^\circ(R)$ values for the prototypical radicals R = C_2H_5, $i\text{-}C_3H_7$, and $t\text{-}C_4H_9$ continue to receive much attention[1-11] in view of persisting discrepancies between data derived from iodination studies as a primary standard

$$RH + I \rightleftharpoons R + HI \qquad (1,-1)$$

incorporating an assumed activation energy for the opposing reaction, $E_{-1} \approx 1 \pm 1$ kcal mol^{-1},[10] and other equilibria not involing the halogen.[1,2,5,6] In general, the earlier iodination studies have yielded "lower" $\Delta H_f{}^\circ(R)$ values.

Cumulative evidence[1-4,8,11] and a direct determination of the equilibrium[6] $H + C_2H_4 \rightleftharpoons C_2H_5$ have now established $\Delta H_f{}^\circ{}_{298}(C_2H_5) = 28.4$ kcal mol^{-1}, some 2.5 kcal mol^{-1} higher than the earlier "accepted" value.[10] The situation with respect to the $i\text{-}C_3H_7$ and $t\text{-}C_4H_9$ radicals is less resolved, though here, again, a trend to higher values may be indicated.[5,7,8] The range of literature values encompasses $\Delta H_f{}^\circ{}_{298}(i\text{-}C_3H_7) = 18.2$ to 22.3 kcal mol^{-112} and $\Delta H_f{}^\circ{}_{298}(t\text{-}C_4H_9) = 7.6$ to 12.4 kcal mol^{-1}.[5,7-10] It is worthy of note that the values at the upper end of the range have profound implications on heretofore low-barrier hydrogen atom transfer processes (e.g., R + HBr → RH + Br) in that they predict negative activation energies (!).[7-9] The highest enthalpy of formation values for $i\text{-}C_3H_7$ and $t\text{-}C_4H_9$ have been derived by Tsang[5] from an analysis of a series of nonhalogen kinetic systems, which, when combined with corresponding kinetic data for the reverse reactions, yielded equilibrium constants for the two processes (R = $i\text{-}C_3H_7$, $t\text{-}C_4H_9$):

$$R \underset{k_a}{\overset{k_d}{\rightleftharpoons}} \text{olefin} + H \qquad (2)$$

$$R_2 \underset{k_c}{\overset{k'_d}{\rightleftharpoons}} 2R \qquad (3)$$

Russell et al.[8] have noted that the calculated values of $\Delta H_f{}^\circ(i\text{-}C_3H_7)$ from five kinetic studies related to process 2 are about 1 kcal mol^{-1} higher than those evaluated from three kinetic studies related to the equilibrium process 3. A closer scrutiny of Tsang's evaluation revealed an apparently propagated error for process 2. The purpose of this communication is to correct said error and to recalculate $\Delta H_f{}^\circ{}_{298}(i\text{-}C_3H_7)$ incorporating the latest computed barriers of internal rotation.[13]

Evaluation and Discussion

Tsang evaluated the equilibrium constant for process 2 by combining literature rate ratios (corrected to the high-pressure limit): rate 2/[rate -3]$^{1/2}$ = (rate C_3H_6 production)/[rate 2,3-DMB production)$^{1/2}$ = $k_d{}^\infty/k_c{}^{1/2}$, with independently determined rate constants for isopropyl radical combination (k_c), and hydrogen addition to propene (k_a); thus $K_p = (k_d{}^\infty/k_c{}^{1/2})(k_c{}^{1/2}/k_a)R'T$. Since the determination of relative rate constants is usually more accurate than their absolute measurements, the computed K_p and hence $\Delta H_f{}^\circ(i\text{-}C_3H_7)$ are more susceptible to the choice of k_a and k_c, but less so on the latter because of the square-root dependence.

For k_c Tsang chose to average the room-temperature results of Adachi and Basco[14] ($k_c = 7.7 \times 10^9$ L mol^{-1} s^{-1}), based on flash-photolysis kinetic spectroscopy measurements, with those of Parkes and Quinn[15] who employed the technique of molecular modulation spectroscopy at 300–800 K and observed a small $T^{-1/2}$ temperature dependence, k_c/L mol^{-1} s^{-1} = $(4.8 \pm 1.2)10^9 \times (300/T)^{1/2}$, which was also adopted by Tsang. For the addition reaction Tsang lists k_a/L mol^{-1} s^{-1} = $6.1 \times 10^9 \exp(-609/T)$ which he attributes to Harris and Pitts.[16] In fact, the latter authors did not determine a rate constant for H-addition to the terminal olefinic position, but reported a total rate constant based on flash-photolysis resonance fluorescence measurements. The above expression for k_a is quoted by Harris and Pitts (their Table IV) and is due to Kurylo et al.[17] However, a recalculation of log K_p for reaction 2 using the k_a from Kurylo et al. for the five systems listed in Table I (system II) of Tsang's paper gives somewhat lower values. Tsang's log K_p values can be approximately reconciled with k_a/L mol^{-1} s^{-1} = $3.25 \times 10^9 \exp(-629/T)$, an expression calculable from the second entry in Table IV of Harris and Pitts[16] and attributed to Wagner and Zellner.[18] Unfortunately, in ref 16 the A factor is misquoted; Wagner and Zellner reported k_a/L mol^{-1} s^{-1} = $(5.4 \pm 0.6)10^9 \exp[-(629 \pm 50)/T]$ which, within error limits, is in excellent agreement with the Arrhenius parameters of Kurylo et al.[17], k_a/L mol^{-1} s^{-1} = $(6.13 \pm 0.16)10^9 \exp[-(609 \pm 6)/T]$. Recalculation of the data for process 2 in ref 5 using the latter expression yields lower $\Delta H_f{}^\circ(i\text{-}C_3H_7)$ values, which, in general, agree well with those computed[5] for process 3 (but see below).

The evaluation of $\Delta H_f{}^\circ{}_{298}(R)$ by the third-law method requires entropy and heat capacity data for the species involved. For the isopropyl radical the vibrational assignment is incomplete.[19] Tsang recalculated the entropies for $i\text{-}C_3H_7$ as a function of temperature using the group frequency assignment and (presumably) structural data of Purnell and Quinn,[20] with the difference that he treated

---

[1] Tsang, W. *Int. J. Chem. Kinet.* **1978**, *10*, 821.

[2] Cao, J.-R.; Back, M. H. *Int. J. Chem. Kinet.* **1984**, *16*, 961.

[3] Castelhano, A. L.; Marriott, P. R.; Griller, D. *J. Am. Chem. Soc.* **1981**, *103*, 4262.

[4] Castelhano, A. L.; Griller, D. *J. Am. Chem. Soc.* **1982**, *104*, 3655.

[5] Tsang, W. *J. Am. Chem. Soc.* **1985**, *107*, 2872.

[6] Brouard, M.; Lightfoot, P. D.; Pilling, M. J. *J. Phys. Chem.* **1986**, *90*, 445.

[7] Russell, J. J.; Seetula, J. A.; Timonen, R. S.; Gutman, D.; Nava, D. F. *J. Am. Chem. Soc.* **1988**, *110*, 3084.

[8] Russell, J. J.; Seetula, J. A.; Gutman, D. *J. Am. Chem. Soc.* **1988**, *110*, 3092.

[9] Müller-Markgraf, W.; Rossi, M. J.; Golden, D. M. *J. Am. Chem. Soc.* **1989**, *111*, 956.

[10] McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

[11] Parmar, S. S.; Benson, S. W. *J. Am. Chem. Soc.* **1989**, *111*, 57.

[12] Luo, Y.-R.; Benson, S. W. *J. Phys. Chem.* **1989**, *93*, 3304.

[13] Pacansky, J.; Yoshimine, M. *J. Phys. Chem.* **1987**, *91*, 1024.

[14] Adachi, H.; Basco, N. *Int. J. Chem. Kinet.* **1981**, *13*, 367.

[15] Parkes, D. A.; Quinn, C. P. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 1953.

[16] Harris, G. W.; Pitts, J. N., Jr. *J. Chem. Phys.* **1982**, *77*, 3995.

[17] Kurylo, M. J.; Peterson, N. C.; Braun, W. *J. Chem. Phys.* **1971**, *54*, 4662.

[18] Wagner, H. Gg.; Zellner, R. *Ber. Bunsenges. Phys. Chem.* **1972**, *76*, 440.

[19] Pacansky, J.; Coufal, H. *J. Chem. Phys.* **1980**, *72*, 3298.

0002-7863/89/1511-9030$01.50/0

Table I. Evaluation of K_p for the Process $C_3H_7 \rightleftharpoons C_3H_6 + H$ from Kinetic Data

system[a]	radical source	ref	T_m, K[b]	$k_d^\infty/k_c^{1/2}$,[c] (mol/L s)$^{1/2}$	k_c,[d] L/(mol s)	k_a,[e] L/(mol s)	log K_p
II.3	propane (Hg-sensitized)	21	600	9.90_0 (−6)	4.24 (+9)	2.22 (+9)	-7.85_5
II.4	propane (Hg-sensitized)	22	600	1.03_6 (−5)			-7.82_5
II.1	$(i\text{-}C_3H_6D)_2CO$ (photolysis)	23	700	6.58_0 (−4)	3.93 (+9)	2.57 (+9)	-6.03_5
II.2	$i\text{-}C_3H_7CHO$ (photolysis)	24	700	8.46_2 (−4)			-5.92_6
II.5	propane (azomethane sensitized)	25	750	3.05_2 (−3)	3.79 (+9)	2.72 (+9)	-5.37_1

[a] Numbers refer to Table I in ref 5. [b] Mean temperature of decomposition study. [c] From rate expression in ref 5 and Tsang's assessment of k_d/k_d^∞. [d] k_c/L mol^{-1} s^{-1} = $6 \times 10^9 (300/T)^{1/2}$ as assessed in ref 5. [e] k_a/L mol^{-1} s^{-1} = $(6.13 \pm 0.16)10^9 \exp[-(609 \pm 6)/T]$ from ref 17.

Table II. Heat of Formation of Isopropyl Radical[a] at 298 K

V_0,[b] cal mol^{-1}	ref	$\Delta H_f°_{298}$(R),[c] kcal mol^{-1}	Δ,[d] kcal mol^{-1}
free (2)	5	21.6	0.3
800 (2)	13	21.4	0.3
1080 (2)	13	21.2	0.3
1980 (2)	20	20.7	0.3
3400 (2)	26	20.0	0.3

[a] Kinetics/third law evaluation. Spectroscopic assignments from ref 5. Frequencies (cm^{-1}) 3100 (1), 2960 (6), 1440 (6), 1300 (1), 1200 (1), 990 (4), 950 (1), 397 (1), 367 (1); $I_AI_BI_C = 2.67 \times 10^{-115}$ g^3 cm^6, $\sigma = 2$; internal rotation, 2 rotors (V_0), $I = 4.2 \times 10^{-40}$ g cm^2, symmetry 3. [b] Barrier to internal rotation. [c] Mean value from five kinetic systems (see Table I). [d] Average deviation.

the two CH_3 tops of isopropyl as free rotors, whereas Purnell and Quinn assumed each rotor to be hindered by a 3-fold cosine barrier with V_0 = 1980 cal mol^{-1}. Thus, Tsang calculates slightly higher $S°(i\text{-}C_3H_7)$ values which translates into a somewhat higher radical heat of formation. Recently, Pacansky and Yoshimine[13] reported a theoretical geometry optimization of $i\text{-}C_3H_7$ and computed a 3-fold potential barrier for the single methyl internal rotation of V_0 = 1.08 and 0.8 kcal mol^{-1} for rigid and relaxed motions, respectively, and correspondingly a 3-fold potential function of 2.27 and 1.05 kcal mol^{-1} for the in-phase double internal rotation. These low barriers have little effect on the calculated $\Delta S°_T$ values for process 2 at the elevated temperatures of the kinetic studies, but do affect the heat capacity corrections to 298 K with the result of further lowering $\Delta H_f°_{298}(i\text{-}C_3H_7)$.

Table I lists the recalculated log K_p values from kinetic data at the midpoint of the temperature range in the decomposition studies.[5] To provide ready contact with ref 5, the first two columns identify the system and the method used, and give reference to the original literature[21-25]

Table II lists the mean $\Delta H_f°_{298}$(R) values derived from the five kinetic studies for the free CH_3-rotor model and four hindered rotor models suggested in the literature.[13,20,26] In these calculations we have used the familiar relations

$$\Delta H°_T(2) = -RT \ln K_p + T\Delta S°_T(2)$$

$$\Delta H°_{298}(2) = \Delta H°_T(2) - \langle \Delta C_p° \rangle (T - 298)$$

$$\Delta H_f°_{298}(R) = \Delta H_f°_{298}(H) + \Delta H_f°_{298}(C_3H_6) - \Delta H°_{298}(2)$$

The thermodynamic functions for H and C_3H_6 were taken from standard tabulations.[27,28] The entropy and heat capacity of $i\text{-}C_3H_7$ as a function of temperature were computed from the spectroscopic information listed by Tsang[5] for the free rotor model. Appropriate corrections[29] were then applied for the hindered rotation models.

A comparison of the enthalpy of formation for the free rotor model with Tsang's evaluation shows no dramatic changes, but it narrows the gap between $\Delta H_f°(i\text{-}C_3H_7)$ values evaluated from processes 2 and 3. In the latter group one reported value is anomalously high (Table IV, II.2, ref 5). Recalculation using the rate constant for 2,3-dimethylbutan (DMB) decomposition from the original literature[30] and the well-known thermodynamic functions for DMB[31] yields $\Delta H_f°_{300}(i\text{-}C_3H_7)$ = 20.6 kcal mol^{-1} instead of the reported value[5] of 22.1 kcal mol^{-1}.

The results presented in Table II taken in conjunction with the kinetic third-law-based evaluations for process 3 support a value of $\Delta H_f°_{298}(i\text{-}C_3H_7) = 21.0 \pm 0.5$ kcal mol^{-1} where the uncertainty is a conservative estimate. This value is in agreement with very recent other determinations[8,12] and is consistent with a ca. 1 kcal mol^{-1} barrier for internal rotation for each of the two CH_3 groups in isopropyl. In the light of the ab initio computations of hindered internal rotation barriers,[13] the 3400 cal mol^{-1} value employed by Burcat[26] seems unrealistically high. In this connection, the use of NASA polynomials[26] for thermochemical calculations involving the isopropyl radical is not recommended. The computed C_p and $S°$ values are significantly lower than those obtained from the spectroscopic data listed in the same reference, and which are almost identical with those employed by Tsang.[5]

In concluding it may be noted, that while the present analysis, which supports the higher $\Delta H_f°(i\text{-}C_3H_7)$ value, points to the excellent internal consistency of a significant volume of kinetic data encompassing processes 2 and 3, it does not resolve the issue with respect to the lower ΔH_f values derived from iodination studies.[3,4,10]

Acknowledgment. The financial support of the Natural Science and Engineering Research Council of Canada is gratefully acknowledged.

Registry No. $i\text{-}C_3H_7$, 2025-55-0.

---

(20) Purnell, J. H.; Quinn, C. P. *J. Chem. Soc.* **1964**, 4049.

(21) Papic, M. M.; Laidler, K. J. *Can. J. Chem.* **1971**, *49*, 549.

(22) Back, R. A.; Takamuku, S. *J. Am. Chem. Soc.* **1964**, *86*, 2558.

(23) Heller, C. A.; Gordon, A. S. *J. Phys. Chem.* **1958**, *62*, 709.

(24) Kerr, J. A.; Trotman-Dickenson, A. F. *Trans. Faraday Soc.* **1959**, *55*, 921.

(25) Camilleri, P.; Marshall, R. M.; Purnell, H. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 1491.

(26) Burcat, A. In *Combustion Chemistry*; Gardiner, W. C., Jr.; Ed.; Springer-Verlag: New York, 1984; Chapter 8.

(27) JANAF thermochemical Tables, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.* **1971**, *no.* 37.

(28) Chao, J.; Zwolinski, B. J. *J. Phys. Chem. Ref. Data* **1975**, *4*, 251.

(29) Lewis, G. N.; Randall, M. *Thermodynamics*, 2nd ed.; McGraw-Hill: New York, 1961 (revised by K. S. Pitzer and L. Brewer).

(30) Bull, K. R.; Marshall, R. M.; Purnell, J. H. *Proc. R. Soc. London, Ser. A* **1975**, *342*, 259.

(31) Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*, Wiley: New York, 1969.