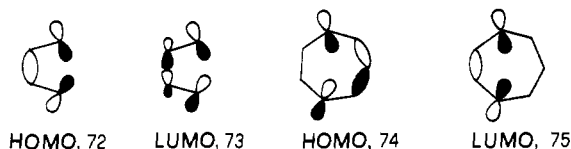


ences in the strain energies in both systems, electronic factors have been made responsible for this contrasting behavior.⁵¹ Due to the strong π/σ -interactions in 70, the HOMO (72) is found to be bonding (π^+) and the LUMO (73) antibonding with respect to a π/π - and π^*/π^* -interaction^{11a} (see below).



In 68, however, the propano bridges overrule the effect of the ethano bridges as discussed for 16 and thus the phases are reversed, i.e., the HOMO (74) is antibonding and the LUMO (75) is bonding with respect to a π/π - and π^*/π^* -interaction, respectively. Thus the excitation of an electron in 68 from the HOMO (74) to the LUMO (75) increases the bonding between the π -units, and therefore the [2 + 2]cycloaddition in this molecule should be favored.

(52) Criegee, R. *Angew. Chem., Int. Ed. Engl.* 1962, 1, 519. Iwamura, H.; Morio, K.; Kihara, H. *Chem. Lett.* 1973, 457.

Conclusion

The mode of thinking of most chemists with respect to the interaction of π -moieties that are not directly connected with each other is a through-space one and disregards the σ -frame. From this it seems logical that the interaction of π -systems depends on their mutual distance and orientation only. Experimental investigations together with model calculations have revealed that this view is too simple. The σ -frame not only is used to fix the π -units but also contributes considerably. As it turns out, the most important parameters of the σ -frame are its length and the energies of the orbitals associated with the σ -chain. To judge the influence of the length of the σ -frame, a simple rule emerges: a bridge with two carbon atoms narrows the gap between π_+ and π_- , while a bridge with three carbon centers enlarges it (see Figure 2). Usually the effect of a propano bridge overrules that of an ethano bridge. The strong influence of the bridge affects the reactivity considerably. This should be and has been observed in those cases where a switch of the frontier orbitals occurs within a series of similar molecules (e.g., 15-19 or 36-40). Recent experiments in the series of cyclic diacetylenes¹⁵ have demonstrated this prediction.

We are grateful to all the co-workers and colleagues whose names appear in the references. We thank the Fonds der Chemischen Industrie, the Deutsche Forschungsgemeinschaft, and the BASF Aktiengesellschaft for continuous support.

The Controversial Heat of Formation of the *t*-C₄H₉ Radical and the Tertiary C-H Bond Energy

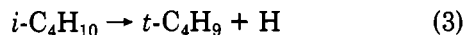
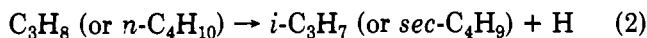
DAVID GUTMAN

Department of Chemistry, Catholic University of America, Washington, D.C. 20064

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Introduction

Accurate heats of formation of the alkyl radicals are of value for a number of reasons. For example, they are needed to determine the primary, secondary, and tertiary C-H bond dissociation energies, i.e., DH°_{298} for the following process:¹⁻³



David Gutman attended both UCLA and UC, Berkeley, receiving his B.S. from Berkeley in 1960. It was there, in Harold S. Johnston's physical chemistry class, that he became intrigued with the properties of as well as the chemical kinetics of free radicals, subjects that continue to fascinate him to this date. He studied high-temperature kinetics with a shock tube under the direction of R. Linn Belford at U. Illinois, Urbana, receiving his Ph.D. in 1965. Then he joined the chemistry faculty at the Illinois Institute of Technology, rising to the rank of Professor. In 1988, he moved to The Catholic University of America, where he is chair of the Chemistry Department and continues his studies on the kinetics and thermochemistry of the reactions of polyatomic free radicals, particularly those involved in hydrocarbon combustion, tropospheric processes, industrial synthesis, and most recently, gas-surface catalysis.

These and other bond energies are invaluable in mechanistic chemistry because they provide the means to determine heats of formation of reaction intermediates and transition states (known or postulated).² When this thermochemical information is accurately known, it yields useful enthalpic criteria that, together with laboratory measurements (such as enthalpies of activation), can be used to discriminate between plausible reaction mechanisms.^{2,4-7} When bond energies are inaccurate, their use for this same purpose can lead to erroneous and sometimes unusual conclusions.

A major controversy arose from the use of widely accepted low C-H bond energies to calculate the heats

- (1) Kerr, J. A. *Chem. Rev.* 1966, 66, 465.
- (2) Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1976.
- (3) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* 1982, 33, 493.
- (4) Doering, W. v. E. *Proc. Natl. Acad. Sci. U.S.A.* 1981, 78, 5279.
- (5) Bergman, R. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1, Chapter 5.
- (6) Berson, J. A. *Annu. Rev. Phys. Chem.* 1977, 28, 111.
- (7) Berson, J. A. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic: New York; Vol. 1, p 324.

Table I
Recommended Heats of Formation (298 K) of Small Alkyl Radicals Used To Determine C-H Bond Energies^{a,b}

radical (R)	recommendtn based on studies of R + HX ⇌ RH + X equilibria		recommendatn based on studies of dissocn/recombinatn equilibria: Tsang (1978, 1985) (refs 8, 9)	recent determinatn
	Golden and Benson (1969) (ref 10) ^c	McMillen and Golden (1982) (ref 3)		
C ₂ H ₅	107 ± 4	108 ± 4	119 ± 2	119, ¹³ 120, ¹⁴ 118, ¹⁵ 119 ¹⁶
<i>i</i> -C ₃ H ₇	76 ± 4	76 ± 4	88 ± 2.5 ^d	88 ¹⁴
<i>sec</i> -C ₄ H ₉	54	54 ± 4	71 ± 1.6	67 ³³
<i>t</i> -C ₄ H ₉	33 ± 4	36 ± 4	51.7 ± 2.2 (0) ^e 46.2 ± 2.2 (10) ^e	48.6, ²⁰ 48 ²¹ 38.5, ¹⁹ 41, ³⁴ ≤45 ³⁵

^aEnergy units used are kJ mol⁻¹. ^bError limits are those indicated by the authors. (In the case of ref 10 the error limits are those recommended by the authors for the C-H bond energies derived from these heats of formation.) ^cAlso recommended by O'Neal and Benson (1973).¹¹ ^dCorrected computation.¹² ^eBecause of the uncertainty in the CH₃ rotation barrier in *t*-C₄H₉, Tsang provided maximum and minimum recommended heats of formation based on third law calculations using the minimum (0) and maximum (10) likely values of the rotation barrier in the calculation of the entropy of the radical. The *t*-C₄H₉ heat of formation is indicated to be between the two recommended values.

of formation of diradical structures believed formed during thermal reorganizations (such as *cis*-*trans* isomerizations).⁴⁻⁷ (The problem this created and its resolution have been vividly described by Doering.⁴) The whole notion of the existence of *metastable* diradical intermediates (i.e., ones with 15-20 kJ mol⁻¹ barriers to ring closure to re-form one of the stable isomers) arose from the need to reconcile the experimental activation energies for these isomerizations with the calculated heats of formation of the diradical structures. The use of prevailing C-H bond energies (which are ≈ 10 kJ mol⁻¹ too low) resulted in calculated heats of formation of diradical intermediates that were typically 15-20 kJ mol⁻¹ low (a diradical can be hypothetically formed by breaking two C-H bonds in a stable molecule). Measured activation energies of thermal rearrangements were noticeably higher (15-20 kJ mol⁻¹) than the apparent energy needed to form the diradical intermediates. It became necessary to hypothesize an energy barrier to ring closure of the diradical in order to reconcile this energy difference with a diradical mechanism. The need for and belief in metastable diradical intermediates in *cis*-*trans* isomerizations have diminished substantially as more accurate C-H bond energies are now providing diradical heats of formation that are in accord with measured activation energies for thermal rearrangements.

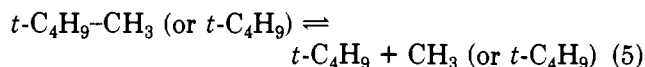
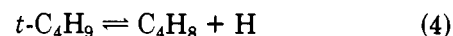
Today there is a near convergence of opinions regarding the heats of formation of C₂H₅ and *i*-C₃H₇ (and hence the values of the primary and secondary C-H bond energies). However, the *t*-C₄H₉ heat of formation (and the tertiary C-H bond energy) remains a controversial topic. Recent determinations continue to differ by as much as 10 kJ mol⁻¹.

In this Account, the principal ways in which the heat of formation of the *t*-C₄H₉ radical has been obtained are reviewed. It will be shown that differences between reported values have usually resulted not from inadequate experiments but primarily from inaccuracies in the assumed information needed to perform the thermochemical calculations. Values of the *t*-C₄H₉ heat of formation recalculated by using current knowledge of the formerly assumed information are presented. These new values are in close agreement with each other as well as with our recent direct determination (also discussed here), which did not require the use of any of the formerly used assumptions. The controversy surrounding the *t*-C₄H₉ heat of formation and the last of

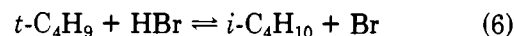
the C-H bond energies appears resolved.

The Conflicting Determinations of the *t*-C₄H₉ Heat of Formation

Until quite recently, studies of dissociation-recombination equilibria^{8,9} such as those in reactions 4 and 5, which involve the *t*-C₄H₉ radical, have yielded alkyl



radical heats of formation that are between 8 and 12 kJ mol⁻¹ higher than those that have come from investigations of equilibria involving reactions of the alkyl radicals with the hydrogen halides (HX),^{3,10,11} e.g.,



Tsang^{8,9} has conducted a comprehensive data analysis of kinetic studies related to dissociation-recombination equilibria and has recommended heats of formation for the alkyl radicals (R) that are consistent with these data. Golden and Benson,¹⁰ O'Neal and Benson,¹¹ and McMillen and Golden³ have likewise reviewed kinetic studies involved in R + HX ⇌ RH + X equilibria and have recommended another set of free-radical heats of formation that can be derived from the results of the latter studies. The disparate recommendations for the alkyl radicals from which the C-H bond energies are derived are presented in Table I.

In recent years, more direct experiments involving both kinds of equilibria have yielded new values of the C₂H₅¹³⁻¹⁶ and *i*-C₃H₇¹⁴ heats of formation that agree very well with Tsang's recommended values.^{8,9} The recent

(8) Tsang, W. *Int. J. Chem. Kinet.* **1978**, *10*, 821.

(9) Tsang, W. *J. Am. Chem. Soc.* **1985**, *107*, 2872.

(10) Golden, D. M.; Benson, S. W. *Chem. Rev.* **1969**, *69*, 125.

(11) O'Neal, H. E.; Benson, S. W. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 2, Chapter 17.

(12) Tschuikow-Roux, E.; Chen, Y. *J. Am. Chem. Soc.* **1989**, *111*, 9030.

(13) Brouard, M.; Lightfoot, P. D.; Pilling, M. J. *J. Phys. Chem.* **1986**, *90*, 445.

(14) Russell, J. J.; Seetula, J. A.; Gutman, D. *J. Am. Chem. Soc.* **1988**, *110*, 3092.

(15) Parmer, S. S.; Benson, S. W. *J. Am. Chem. Soc.* **1989**, *111*, 57.

(16) Pacey, P. D.; Wimalasena, J. H. *J. Phys. Chem.* **1984**, *88*, 5657.

low¹⁷⁻¹⁹ and high²⁰ values of the $t\text{-C}_4\text{H}_9$ heat of formation have actually come from studies of the same systems, reactions 6 and 7.

Assumed or Calculated Information Used To Obtain the $t\text{-C}_4\text{H}_9$ Heat of Formation from the Results of Kinetic Studies

The two principal pieces of information that have been assumed or estimated in former studies of the thermochemistry of $t\text{-C}_4\text{H}_9$ are the activation energies of the $t\text{-C}_4\text{H}_9 + \text{HX}$ reactions^{3,10,11} and the entropy of the $t\text{-C}_4\text{H}_9$ radical.^{3,8,9}

1. Activation Energies of the $t\text{-C}_4\text{H}_9 + \text{HX}$ Reactions. In "second law" determinations of the $t\text{-C}_4\text{H}_9$ heat of formation based on studies of reactions 6 and 7, the reaction enthalpy change is obtained directly from the difference between the activation energies of the forward and reverse reactions.^{10,11} The determination of this enthalpy change yields the $t\text{-C}_4\text{H}_9$ heat of formation because the heats of formation of the other reactant and the products of reactions 6 and 7 are accurately known.

Until recently, these studies combined a measured activation energy for the $\text{X} + i\text{-C}_4\text{H}_{10}$ reaction with an assumed activation energy for the $t\text{-C}_4\text{H}_9 + \text{HX}$ reaction^{10,11} to obtain the enthalpy change of the reaction. Reactions of polyatomic free radicals with the hydrogen halides were known to be rapid reactions,¹¹ and it has been the practice to assume a small positive generic activation energy near 0 for all such reactions with a particular hydrogen halide. (Negative activation energies were not considered possible for what appear to be simple H atom metatheses.) The assumed values were $4 \pm 4 \text{ kJ mol}^{-1}$ for all radical + HI reactions (which includes 0 within the uncertainty limits) and $8 \pm 4 \text{ kJ mol}^{-1}$ for all radical + HBr reactions (the higher value accounting for the fact that radical + HBr reaction rate constants are somewhat below those of radical + HI reactions).^{10,11}

Recently, we investigated the kinetics of both reactions 6 and 7.^{20,21} These elementary reactions were isolated for direct study in a heatable tubular reactor coupled to a photoionization mass spectrometer. The $t\text{-C}_4\text{H}_9$ radicals were produced homogeneously in the reactor using pulsed UV laser photolysis, and $t\text{-C}_4\text{H}_9$ decay profiles in the presence and absence of HX were monitored in time-resolved experiments using the photoionization mass spectrometer. Reaction rate constants were measured as a function of temperature.

In these studies it was discovered that both reactions 6 and 7 have activation energies outside of the assumed ranges. In fact, both have significant negative activation energies, $-6.3 \pm 0.8 \text{ kJ mol}^{-1}$ for the $t\text{-C}_4\text{H}_9 + \text{HI}$ reaction²¹ and $-5.8 \pm 0.9 \text{ kJ mol}^{-1}$ for the $t\text{-C}_4\text{H}_9 + \text{HBr}$ reaction.²⁰

Very recently, these surprising findings were confirmed. Richards et al.²² studied the kinetics of both reactions 6 and 7 using a different experimental pro-

(17) Rossi, M. J.; Golden, D. M. *Int. J. Chem. Kinet.* 1979, 11, 969.

(18) Rossi, M. J.; Golden, D. M. *Int. J. Chem. Kinet.* 1983, 15, 1283.

(19) Müller-Markgraf, W.; Rossi, M. J.; Golden, D. M. *J. Am. Chem. Soc.* 1989, 111, 956.

(20) Russell, J. J.; Seetula, J. A.; Timonen, R. S.; Gutman, D.; Nava, D. F. *J. Am. Chem. Soc.* 1988, 110, 3084.

(21) Seetula, J. A.; Russell, J. J.; Gutman, D. *J. Am. Chem. Soc.* 1990, 112, 1347.

(22) Richards, P. D.; Ryther, R. J.; Weitz, E. *J. Phys. Chem.* 1990, 94, 3663.

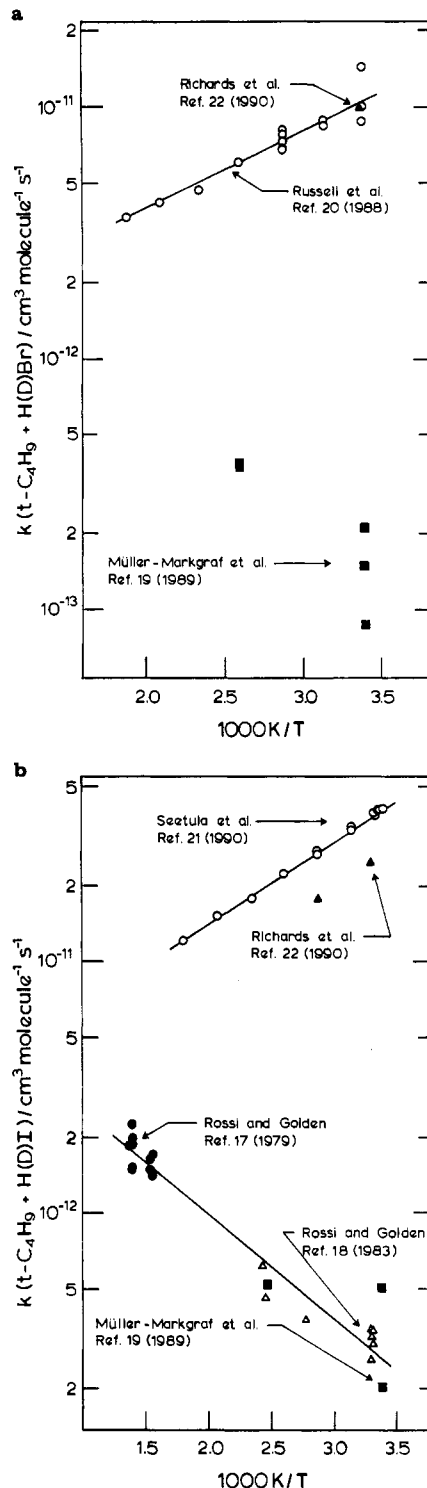


Figure 1. Arrhenius plots of $t\text{-C}_4\text{H}_9 + \text{HX}$ (and DX) rate constants: (a) $t\text{-C}_4\text{H}_9 + \text{HBr}$ (and DBr) reaction; (b) $t\text{-C}_4\text{H}_9 + \text{HI}$ (and DI) reaction. (The line connecting the rate constants of Rossi and Golden is the Arrhenius expression reported by the authors).¹⁸

cedure and a different diagnostic technique. They monitored the growth of the product, $i\text{-C}_4\text{H}_{10}$, in time-resolved experiments using a tunable infrared diode laser probe. The rate constants obtained by Richards et al. for both reactions are in very good agreement with the one we determined (see Figure 1), and the activation energy they obtained for the $t\text{-C}_4\text{H}_9 + \text{HI}$ reaction is identical with the one we determined. (They only investigated the $t\text{-C}_4\text{H}_9 + \text{HBr}$ reaction at ambient temperature and therefore did not obtain its activation energy.)

Acceptance of these experimental results has been slow in part because significant negative activation energies for direct H atom transfer reactions are regarded as being "without precedent",^{19,23} "disconcerting",³ "very unlikely",²⁴ and "controversial".²⁵ We sympathize with these opinions and concerns. However, we interpret the "strangeness" of these experimental results in another way, as clues that the apparent and presumed reaction mechanism is incorrect. We have suggested that the observations are strong indications of a more complex, multistep process.^{14,20,21} The mechanism we have proposed that accounts for the experimental results involves the following steps: attraction of the $t\text{-C}_4\text{H}_9$ radical to the halogen end of the HX molecule to form a bound $t\text{-C}_4\text{H}_9\text{XH}$ complex followed by decomposition by one of two paths, direct dissociation to re-form the original reactants (via a loose transition state) or rearrangement via internal rotation of HX (followed by decomposition into the observed new products, $i\text{-C}_4\text{H}_{10} + \text{X}$) via a tight transition state. That such a mechanism can, under appropriate conditions, yield the observed rate constants and negative activation energies for thermal rate constants that characterize the overall process has been discussed in detail by Mozurkewich and Benson.²⁶

McEwen and Golden have now used our suggested mechanism to calculate overall thermal rate constants for the $t\text{-C}_4\text{H}_9 + \text{HI} \rightarrow i\text{-C}_4\text{H}_{10} + \text{I}$ reaction.²⁷ RRKM calculations were performed to obtain rate constants for the individual steps. Using reasonable transition-state properties, they were able to reproduce both the magnitudes of the thermal rate constants and the observed negative activation energy.

The experimental²⁰⁻²² results taken together indicate that the rate constants of reactions 6 and 7 are now established within the stated accuracy limits. The recent calculations of McEwen and Golden provide support for the proposal that these reactions are in fact complex processes involving the formation of a bound intermediate. This kinetic information is now available for the relevant thermochemical calculations.

2. Entropy of $t\text{-C}_4\text{H}_9$. Many if not most of the determinations of the $t\text{-C}_4\text{H}_9$ heat of formation have involved "third law" calculations. In these studies, a chemical equilibrium involving the $t\text{-C}_4\text{H}_9$ radical was characterized at a single temperature. In particular, the ratio of rate constants of the forward and reverse reactions was determined at one temperature T to obtain ΔG°_T . The entropy change of the reaction was then calculated and used together with the ΔG°_T determination to obtain the enthalpy change of the equilibrium under study. As in section 1 above, the $t\text{-C}_4\text{H}_9$ heat of formation was then obtained from this enthalpy change by using the known heats of formation of the other species involved in the reaction.

In Tsang's comprehensive evaluation of the many kinetic studies pertaining to dissociation-recombination equilibria including reactions 4 and 5, he clearly demonstrates that little disagreement exists between the $t\text{-C}_4\text{H}_9$ free energies of formation which can be derived directly from experiment.⁹ He showed that where

disagreements had existed, they were usually due to the different values of the $t\text{-C}_4\text{H}_9$ entropy used in the thermochemical calculations.

Differences in the calculated entropy of $t\text{-C}_4\text{H}_9$ have arisen largely from different estimates of the two most sensitive uncertain parameters in the entropy calculation, the low pyramidal deformation vibration frequency (200–850 cm^{-1}) and the potential-energy barrier for the internal rotation of the CH_3 groups (0–10 kJ mol^{-1}). Prior to 1984, selection of values for these two parameters was based solely on conjecture.

The entropy of $t\text{-C}_4\text{H}_9$ has now been determined both theoretically and experimentally. In an extensive series of experimental and theoretical studies ending in 1986, Pacansky and co-workers²⁸⁻³⁰ obtained a complete description of the structure and internal motions of the $t\text{-C}_4\text{H}_9$ radical. It included a pyramidal frequency of 158 cm^{-1} and an internal CH_3 rotation barrier of 6.3 kJ mol^{-1} . Use of Pacansky's $t\text{-C}_4\text{H}_9$ structure, vibration frequencies, and internal rotation barrier to calculate the entropy of $t\text{-C}_4\text{H}_9$ at 298 K yields the value $314 \pm 10 \text{ J mol}^{-1} \text{ K}^{-1}$.

In our detailed investigation of the kinetics of reaction 6,²⁰ we determined both the heat of formation of the $t\text{-C}_4\text{H}_9$ radical and its entropy directly from the measured rate constants without the use of any assumptions. The values obtained at 298 K are $48.6 \pm 1.7 \text{ kJ mol}^{-1}$ for the heat of formation and $316 \pm 7 \text{ J mol}^{-1} \text{ K}^{-1}$ for the entropy. The entropy is in excellent agreement with Pacansky's theoretical determination. (The heat of formation is discussed below.)

The very close agreement between the only direct experimental and only detailed theoretical determinations of the $t\text{-C}_4\text{H}_9$ entropy indicates that its value is also now established, certainly within the stated error limits. These determinations are also available for future thermochemical calculations of the $t\text{-C}_4\text{H}_9$ heat of formation.

Redeterminations of the $t\text{-C}_4\text{H}_9$ Heat of Formation from the Results of Prior Investigations

We have used the experimentally determined activation energies for the $t\text{-C}_4\text{H}_9 + \text{HX}$ reactions and the determinations of the entropy of this radical ($315 \pm 6 \text{ J mol}^{-1} \text{ K}^{-1}$, the mean of the experimental and theoretical determinations) in new second and third law calculations of its heat of formation. We have repeated thermochemical calculations conducted in previous studies using this current knowledge in place of assumed or less accurate calculated values of this same information. The results are presented in Table II.

There is now extremely close agreement between the determinations of the $t\text{-C}_4\text{H}_9$ heat of formation, not only between values obtained from studies of the same kind of chemical equilibrium (as was demonstrated previously by Tsang and by Golden and co-workers) but now, more importantly, also between values that are derived from kinetic studies of both kinds of equilibria discussed above.

The more accurately calculated values of the $t\text{-C}_4\text{H}_9$ heat of formation based on older kinetic data are in

(23) Miyokawa, K.; Tschuikow-Roux, E. *J. Phys. Chem.* **1990**, *94*, 715.

(24) Islam, T. S. A.; Benson, S. W. *Int. J. Chem. Kinet.* **1984**, *16*, 995.

(25) Chen, Y.; Rauk, A.; Tschuikow-Roux, E. *J. Phys. Chem.*, in press.

(26) Mozurkewich, M.; Benson, S. W. *J. Phys. Chem.* **1984**, *88*, 6429.

(27) McEwen, A. B.; Golden, D. M. *J. Mol. Struct.* **1990**, *224*, 357.

(28) Pacansky, J.; Chang, J. S. *J. Chem. Phys.* **1981**, *74*, 5539.

(29) Schrader, B.; Pacansky, J.; Pfeiffer, U. *J. Phys. Chem.* **1984**, *88*, 4069.

(30) Pacansky, J.; Yoshimine, M. *J. Phys. Chem.* **1986**, *90*, 1980.

Table II
Original Determinations and Recalculations of the Heat of Formation of $t\text{-C}_4\text{H}_9$ (298 K)

reactn or equilibrium investigated	$t\text{-C}_4\text{H}_9$ heat of formatn derived from results of kinetic investigatn ^a	
	orig determinatn	recalcd value
Studies Relating to $t\text{-C}_4\text{H}_9 + \text{HI} \rightleftharpoons i\text{-C}_4\text{H}_{10} + \text{I}^b$		
Bracey, Walsh (1988) ($\text{I} + i\text{-C}_4\text{H}_{10}$)	–	50 ²¹
Teranisi, Benson (1963) ($\text{I} + i\text{-C}_4\text{H}_{10}$)	32 ¹⁰	47 ²¹
Knox, Musgrave (1967) ($\text{I} + i\text{-C}_4\text{H}_{10}$)	37 ¹⁰	50 ²¹
Studies Relating to $t\text{-C}_4\text{H}_9 + \text{HBr} \rightleftharpoons i\text{-C}_4\text{H}_{10} + \text{Br}^c$		
Benson, Kondo, Marshall (1987) ³³ ($\text{Br} + i\text{-C}_4\text{H}_{10}$)	$\leq 45^{35}$	$\leq 51^c$
Russell et al. (1988) ²⁰ ($\text{Br} + i\text{-C}_4\text{H}_{10} \rightleftharpoons \text{HBr} + t\text{-C}_4\text{H}_9$)	48.6 \pm 1.7 ²⁰ (direct determinatn)	
Dissociation-Recombination Equilibria (Reactions 4 and 5)		
Tsang (1985) ⁹ (review of 10 studies)	see Table I	50.1 \pm 2.2 ^c

^a Energy units used are kJ mol⁻¹. ^b References and calculations given in ref 21. ^c See text.

excellent agreement with our recent direct determination. We consider this result as overwhelming evidence that this heat of formation is now accurately determined.

Kinetic Studies of $t\text{-C}_4\text{H}_9 + \text{HX}$ Reactions Using a Well-Stirred Reactor

We review separately a group of three studies of $t\text{-C}_4\text{H}_9 + \text{DBr}$ and $t\text{-C}_4\text{H}_9 + \text{DI}$ reactions conducted by Golden and co-workers¹⁷⁻¹⁹ which all involved the use of a low-pressure well-stirred reactor.^{31,32} The $t\text{-C}_4\text{H}_9$ radical was produced either thermally¹⁷ or photochemically.^{18,19} Taken together, the results obtained provide the principal remaining support for a low (38.5 kJ mol⁻¹)¹⁹ heat of formation for the $t\text{-C}_4\text{H}_9$ radical, in particular, because the conclusions were obtained (in the last two of these investigations^{18,19}) without the use of the assumptions discussed above. These three studies have yielded much lower rate constants of $t\text{-C}_4\text{H}_9 + \text{DX}$ reactions (by as much as a factor of 100) than those obtained in other recent kinetic studies, those of Russell et al.,²⁰ Seetula et al.,²¹ and Richards et al.²² (see Figure 1). (The disagreement between rate constants obtained by Golden and co-workers, who used DX as a reactant, and those obtained in the other recent studies, which mostly used HX, can be made directly here because the deuterium isotope effect on the thermal rate constant is small²² ($\approx 20\%$) compared to the disagreement (up to 10000%!) in rate constants between these groups of studies.) The results of Golden and co-workers also indicate that both reactions have small positive activation energies^{18,19} that are within the previously assumed ranges.

We believe that this disagreement in rate constants (and hence in the $t\text{-C}_4\text{H}_9$ heat of formation) is caused by the neglect of heterogeneous loss of $t\text{-C}_4\text{H}_9$ in the

Table III
Comparison of Measured and Calculated Slopes of Lines through Data of Müller-Markgraf, Rossi, and Golden (Plotted as $1/f$ vs $10^{15}/F_{\text{DX}}$)¹⁹

reactor escape orifice no./ (diameter, mm)	temp, K	measd slopes	calcd slopes
$t\text{-C}_4\text{H}_9 + \text{DBr}$ Reaction			
1/(1.0)	295	0.365	0.374
2/(1.5)	295	0.730	0.834
3/(2.0)	295	2.46	1.32
2/(1.5)	384	0.545	0.593
3/(2.0)	384	1.26	0.959
$t\text{-C}_4\text{H}_9 + \text{DI}$ Reaction			
2/(1.5)	295	0.247	0.166
3/(2.0)	295	1.51	0.26
2/(1.5)	384	0.311	0.126

well-stirred reactor experiments. In these experiments by Golden and co-workers, only two $t\text{-C}_4\text{H}_9$ loss processes were regarded as important, radical effusion from the reactor and reaction with DBr or DI.^{18,19} First-order heterogeneous loss of $t\text{-C}_4\text{H}_9$ was judged to be of negligible importance, which, in these experiments, would require that it had a first-order rate constant $k_w \ll 1 \text{ s}^{-1}$.

In our investigations, we directly observed *both* the homogeneous $t\text{-C}_4\text{H}_9 + \text{HX}$ reaction and the first-order heterogeneous loss of $t\text{-C}_4\text{H}_9$ radicals and obtained rate constants for both processes.^{20,21} The walls of our reactor were coated with poly(tetrafluoroethylene), the same material that was used to coat the walls of the well-stirred reactor in the last two of the three investigations. Our results would indicate that k_w in the well-stirred reactor experiments of Müller-Markgraf et al. would have been typically 45 s⁻¹ at 295 K and 16 s⁻¹ at 384 K, the two temperatures used in their experiments. Both these values of k_w are $\gg 1 \text{ s}^{-1}$.

We have tested our explanation for the rate constant disparity by determining whether it is possible to reproduce the important experimental observations reported in the most recent of the well-stirred reactor studies (that by Müller-Markgraf et al.¹⁹) using our measured homogeneous ($t\text{-C}_4\text{H}_9 + \text{HX}$) and heterogeneous $t\text{-C}_4\text{H}_9$ (k_w) rate constants. These investigators obtained their $t\text{-C}_4\text{H}_9 + \text{DBr}$ and $t\text{-C}_4\text{H}_9 + \text{DI}$ rate constants from the slopes of lines through data plotted as $1/f$ vs $1/(\text{DX flow rate})$ (f is the fraction of reaction that occurred during the mean residence time). The calculated rate constant is directly proportional to this measured slope. For each of the eight experiments they conducted, we have calculated the slope using the equation provided by the authors¹⁹ that relates the slope to experimental parameters and the homogeneous and heterogeneous $t\text{-C}_4\text{H}_9$ rate constants. There was no adjustable parameter in these calculations! The results of these calculations are given in Table III.

For the larger group of experiments (five of the eight), those from the study of the $t\text{-C}_4\text{H}_9 + \text{DBr}$ reaction, there is exceptionally close agreement between the experimental slopes and those we calculated using our measured rate constants. The average fractional deviation (as a percentage) between the calculated and the measured slopes is 28%. For the three experiments of this group that involved the use of the two smallest escape apertures (no. 1 and 2), the average deviation is far less, only 8%! This agreement was closer than expected considering the experimental uncertainties in

(31) Rossi, M.; King, D. D.; Golden, D. M. *J. Am. Chem. Soc.* **1979**, *101*, 1223.

(32) Spokes, G. N.; Golden, D. M.; Benson, S. W. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 534.

(33) Seetula, J. A.; Gutman, D. *J. Phys. Chem.*, in press.

(34) Holmes, J. L.; Lossing, F. P.; Maccoll, A. *J. Am. Chem. Soc.* **1988**, *110*, 7339.

(35) Benson, S. W.; Kondo, O.; Marshall, R. M. *Int. J. Chem. Kinet.* **1987**, *19*, 829.

the measured slopes, the $\pm 20\%$ uncertainty in our $t\text{-C}_4\text{H}_9 + \text{HBr}$ rate constant, and the fact that the values of k_w used are only typical values. k_w is not strictly constant! It depends on the age and condition of the reactor wall coating. Typically, in our experiments, it increased by as much as 50% during several weeks of experiments.

This ability to quantitatively reproduce the laboratory observations of Müller-Markgraf et al. using the homogeneous $t\text{-C}_4\text{H}_9 + \text{HBr}$ and the heterogeneous $t\text{-C}_4\text{H}_9$ loss rate constants determined in our study of these two processes is strong proof that our explanation for the rate constant disparity is correct. The much lower $t\text{-C}_4\text{H}_9 + \text{DX}$ rate constants obtained by Müller-Markgraf et al. resulted solely from the failure of the investigators to recognize the importance of heterogeneous loss of $t\text{-C}_4\text{H}_9$ in their experiments.

The positive activation energies of the $t\text{-C}_4\text{H}_9 + \text{DX}$ reactions obtained by Golden and co-workers result from the decreasing importance of the heterogeneous loss of $t\text{-C}_4\text{H}_9$ with increasing temperature. Hence, the neglect of this process in the data analysis results in less and less error in the calculated values of k_6 and k_7 as temperature increases. This situation can be seen in Figure 1 where it is apparent that as temperature increases, the rate constants of Golden and co-workers increase and the disparities between their values and those of the other investigators decrease.

Agreement between the experimental and calculated slopes is significantly poorer for the smaller set of experiments conducted by Müller-Markgraf et al. (three of the eight), those that involved the $t\text{-C}_4\text{H}_9 + \text{DI}$ reaction. Agreement is good in only one case (for which the fractional deviation is 49%). For the other two experiments, agreement varies from fair to poor, the fractional deviations being 146% and 480%. It is not

clear how close to expect these latter comparisons to have been. Müller-Markgraf's own data analysis yielded $t\text{-C}_4\text{H}_9 + \text{DI}$ rate constants that differed by 250% between experiments in which only the size of the escape orifice on the well-stirred reactor was changed.

Summary

Evidence has been presented that the controversy surrounding the heat of formation of the $t\text{-C}_4\text{H}_9$ radical is resolved. The recent directly determined value, $\Delta H^\circ_{f,298} = 48.6 \pm 1.7 \text{ kJ mol}^{-1}$, is recommended. It has been shown to be in complete agreement with experimental results of previous studies from which this radical's heat of formation can be derived. This value corresponds to a tertiary C-H bond energy in $t\text{-C}_4\text{H}_{10}$ of $401.2 \pm 1.7 \text{ kJ mol}^{-1}$.

Most previous disagreements with this recommended value were shown to have resulted not from poor experimental techniques or results but rather from inaccuracies in assumed information used in thermochemical calculations, in particular the activation energies of the $t\text{-C}_4\text{H}_9 + \text{HX}$ reactions and the entropy of the $t\text{-C}_4\text{H}_9$ radical. The accurate values of these properties, which are now available from experiment and/or theoretical calculations, were reviewed.

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The Structure of Crystalline Polymers

L. MANDELKERN

Department of Chemistry and Institute of Molecular Biophysics, Florida State University, Tallahassee, Florida 32306

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Introduction

Long-chain molecules can exist in one of two states. Characteristically in the liquid state there is no long-range order and the chain bonds adopt rotational angles

Leo Mandelkern was born in New York City in 1922 and educated in the public schools there. He received his bachelors degree from Cornell University in 1942. After serving for four years in the armed forces, he returned to Cornell, from where he received his Ph.D. in physical chemistry in 1949. From 1949 through 1951 he was a postdoctoral research associate with Prof. Paul J. Flory at Cornell. He then joined the staff of the National Bureau of Standards, and in 1962 he accepted an invitation to join the faculty of The Florida State University as a Professor of Chemistry. He has remained there until the present time. In 1984 he was named R. O. Lawton Distinguished Professor of Chemistry at the university. He received the Arthur S. Flemming Award in 1958, the American Chemical Society Award in Polymer Chemistry in 1975, and the Applied Polymer Science Award in 1989 from the same society. He has also been the recipient of the Mettler Award of the North American Thermal Analysis Society in 1984, the George Stafford Whitby Award of the Rubber Division of the American Chemical Society in 1988, and the Florida Award of the American Chemical Society in 1984.

that are dictated by the rules of statistical mechanics. Hence a random chain structure evolves. The centers of gravity of the individual molecules are also randomly arranged relative to one another. Characteristic of this state is long-range or rubber-like elasticity. However, under appropriate conditions a chain with sufficient structural regularity can spontaneously develop order along a portion of its length. A collection of such chains can then be organized into a three-dimensional array, and the system is said to crystallize. In this, the crystalline state, thermodynamic, spectral, and physical properties are quite different from those in the disordered liquid state. As one example, the polymer has now become relatively inelastic with the elastic modulus increasing by many orders of magnitude. The transformation from one state to the other presents some very interesting problems in phase transitions. An