

$C_{(-)}P_{(-)}$  and  $C_{(+)}P_{(-)}$  isomers. Finally, a similar stereospecific breakdown was observed on passage of soman (neat) through isolated guinea pig skin at ca. 30 °C. Initially ( $t \leq 1$  h), only the  $C_{(-)}P_{(-)}$  and  $C_{(+)}P_{(-)}$  isomers of soman reappeared upon passage through the skin preparation.

Hence, in rat blood and liver homogenates of rats, as well as in guinea pig skin, the  $P_{(+)}$  isomers of soman, which have a low anti-AChE activity, are "detoxified" more rapidly than the highly active  $P_{(-)}$  isomers. It is tempting to speculate that in all these systems the same type of enzyme, i.e., a phosphorylphosphatase,<sup>20,21</sup> is responsible for the observed stereospecificity in the breakdown of the stereoisomers of soman.

**Acknowledgment.** We are indebted to Dr. C. van Hooijdonk and B. I. Ceulen for their performance of the skin penetration experiments and C. van Dijk for her assistance in the enzymological experiments.

(20) Mounter, L. A. In "Handbuch der experimentellen Pharmakologie, Cholinesterases and Anticholinesterase Agents"; Koelle, G. B., Ed.; Springer: Berlin, 1963; p 486.

(21) Frederiksson, T. *Acta Derm.-Venereol.* 1969, 49, 490.

## Heats of Formation of *tert*-Butyl and Ethyl Radicals<sup>1</sup>

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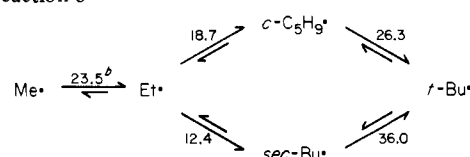
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The C-H bond dissociation energies (BDE) in hydrocarbons are seldom known to better than  $\pm 1$  kcal mol<sup>-1</sup>. This is because they depend upon the heats of formation of alkyl radicals,  $\Delta H_f(R\cdot)$ , which are generally difficult to measure (eq 1). For example,

$$\text{BDE}(R-H) = \Delta H_f(R\cdot) + \Delta H_f(H\cdot) - \Delta H_f(R-H) \quad (1)$$

- (1) Issued as NRCC No. 19513.  
 (2) Teranishi, H.; Benson, S. W. *J. Am. Chem. Soc.* 1963, 85, 2887-2890.  
 (3) Griller, D.; Ingold, K. U. *Int. J. Chem. Kinet.* 1974, 6, 453-456.  
 (4) Choo, K. Y.; Beadle, P. C.; Piszkievicz, L. W.; Golden, D. M. *Ibid.* 1979, 11, 969-976.  
 (5) (a) Marshall, R. M.; Purnell, J. H.; Storey, P. D. *J. Chem. Soc., Faraday Trans 1* 1976, 72, 85-92. Tsang, W. *Int. J. Chem. Kinetics* 1978, 10, 821-837. Walker, J. A.; Tsang, W. *Ibid.* 1979, 11, 867-882. (b) For comments on these studies, see: Taylor, J. E.; Milazzo, T. S. *Ibid.* 1978, 10, 1245-1257. Davis, H. *Ibid.* 1979, 11, 1131-1132. Taylor, J. E. *Ibid.* 1979, 11, 1133.  
 (6) Parks, D. A.; Quinn, C. P. *J. Chem. Soc., Faraday Trans. 1* 1976, 1952-1971.  
 (7) Atri, G. M.; Baldwin, R. R.; Evans, G. A.; Walker, R. W. *J. Chem. Soc., Faraday Trans. 1* 1978, 74, 366-379.  
 (8) Thermochemical data taken from: Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds" Academic Press: New York, 1970.  
 (9) (a) Hiatt, R.; Benson, S. W. *J. Am. Chem. Soc.* 1972, 94, 25-29. (b) *Int. J. Chem. Kinet.* 1972, 4, 151-157. (c) *Ibid.* 1973, 5, 385-396.  
 (10) Traeger, J. C.; McLoughlin, R. G. *J. Am. Chem. Soc.*, in press. The value of  $\Delta H_{f,300}(\text{Me}\cdot) = 34.4 \pm 0.7$  kcal mol<sup>-1</sup> is based upon a combination of new experimental results and a critical review of earlier data. See also: Stull, D. R.; Prophet, H. "JANAF Thermochemical Tables", 2nd Ed., Natl. Stand. Ref. Data Ser. (U.S., Natl. Bur. Stand. 1971, NSRDS-NBS 37. Baghal-Vayjooee, M. H.; Colussi, A. J.; Benson, S. W. *J. Am. Chem. Soc.* 1978, 100, 3214-3215. *Int. J. Chem. Kinet.* 1979, 11, 147-154. Kerr, J. A. *Chem. Rev.* 1966, 66, 465-500. Shaw, R. *J. Phys. Chem. Ref. Data* 1978, 7, 1179-1190.

Scheme I. Equilibrium Constants Measured at 60 °C for Reaction 5<sup>a</sup>



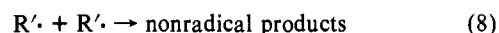
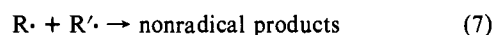
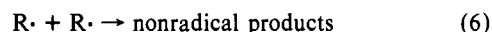
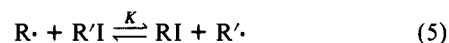
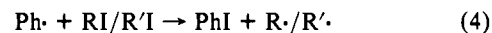
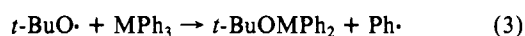
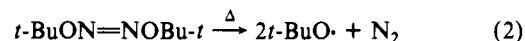
<sup>a</sup> Error  $\pm 10\%$ . <sup>b</sup> Measured at 0 °C.

previously reported values<sup>2-7</sup> of  $\Delta H_{f,300}(t\text{-Bu}\cdot)$  cover the range 6.7-12.9 kcal mol<sup>-1</sup> and give BDE for the simplest tertiary C-H bond, i.e., that in isobutane, as somewhere between 91.2 and 97.4 kcal mol<sup>-1</sup>.<sup>8</sup>

In response to these problems, we have developed a system for measuring the *relative* heats of formation of alkyl radicals, which makes use of a "radical buffer".<sup>9</sup> With this technique, heats of formation of *tert*-butyl and ethyl radicals were measured relative to that of methyl, which serves as a reasonable standard,<sup>10</sup>  $\Delta H_f(\text{Me}\cdot) = 34.4 \pm 0.7$  kcal mol<sup>-1</sup>.

Our approach is based upon measurements of equilibrium constants,  $K$ , for the rapid exchange reactions which take place between alkyl radicals and alkyl iodides<sup>11</sup> (eq 5). Given the entropies of all of the components and the heats of formation of the iodides, a measurement of  $K$  leads to a value of  $\Delta H_f(R\cdot) - \Delta H_f(R'\cdot)$ .

The equilibrium constants,  $K$ , were measured by using EPR spectroscopy. Typically, an isooctane solution containing 0.5 M di-*tert*-butyl hyponitrite, 0.5 M triphenylarsine or triphenylboron, and 0.1-2.0 M of the two alkyl iodides was heated at 60 °C in the spectrometer cavity. The reaction scheme is described in eq 2-8. Relative radical concentrations were measured by double integration of appropriate lines in the EPR spectra.



From the point of view of these experiments, the reaction of phenyl radical with alkyl iodides is essentially irreversible.<sup>12</sup> The exchange reactions between alkyl radicals and alkyl iodides proceed with rate constants  $> 10^5$  M<sup>-1</sup> s<sup>-1</sup>,<sup>11-13</sup> and hence the rates of these reactions are extremely rapid compared with the rates of loss of alkyl radicals by self-reaction, eq 6-8.<sup>9</sup> Therefore, the observed relative concentrations of the radicals are dependent upon the equilibrium constant<sup>14</sup>  $K$ . Moreover, values of  $K$  were independent of both the relative and absolute concentrations of the two iodides when these were varied by a factor of 10.

As an additional safeguard, the equilibria were, in some instances, established by using a second system for radical gener-

(11) Russell, G. A.; Lamson, D. W. *J. Am. Chem. Soc.* 1969, 91, 3967-3968. Lepley, A. R. *J. Chem. Soc., Chem. Commun.* 1969, 64-65. Ward, H. R.; Lawler, R. G.; Cooper, R. A. *J. Am. Chem. Soc.* 1969, 91, 746-748. Lepley, A. R.; Landau, R. L. *Ibid.* 1969, 91, 748-749. Fischer, H. *J. Phys. Chem.* 1969, 73, 3837-3838.

(12) Ward, H. R.; Lawler, R. G.; Cooper, R. A. *Tetrahedron Lett.* 1969, 527-530. Cooper, R. A.; Lawler, R. G.; Ward, H. R. *J. Am. Chem. Soc.* 1972, 94, 545-558.

(13) Lawler, R. G.; Ward, H. R.; Allen, R. B.; Ellenbogen, P. E. *J. Am. Chem. Soc.* 1971, 93, 789-791.

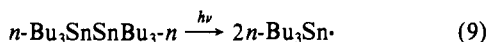
(14) As further evidence, we note that the observed concentrations of R and R' do not reflect the relative rates of phenyl attack upon RI and R'I. See: Danen, W. C.; Tipton, T. J.; Saunders, D. G. *J. Am. Chem. Soc.* 1971, 93, 5186-5189.

Table I. Thermodynamic Parameters Used in the Calculation of  $\Delta H_{f,300}(R\cdot)^a$ 

R'	$K_{300}^b$	$S_{300}^c(R\cdot)$	$S_{300}^c(R'I)$	$\Delta H_{f,300}(R'I)^c$	$\Delta H_{f,300}(R\cdot)$	BDE <sub>300</sub> (R'-H)
Me	1	46.4 <sup>d</sup>	60.5 <sup>e</sup>	3.4 ± 0.3	34.4 <sup>f</sup>	104.4 <sup>f</sup>
Et	20.1	59.2 <sup>d</sup>	70.7 <sup>g</sup>	-2.0 ± 0.4	28.0 ± 1.0 <sup>h</sup>	100.3 ± 1.0
<i>t</i> -Bu	1.67 × 10 <sup>4</sup>	73.0 <sup>i</sup>	82.5 <sup>j</sup>	-17.2 ± 0.3	9.4 ± 1.0 <sup>h</sup>	93.9 ± 1.0

<sup>a</sup>  $\Delta H_f$ , kcal mol<sup>-1</sup>;  $S^\circ$ , cal deg<sup>-1</sup> mol<sup>-1</sup>. <sup>b</sup> For reaction 5, R = Me. <sup>c</sup> From ref 8; see also ref 16. <sup>d</sup> Reference 18. <sup>e</sup> Gelles, E.; Pitzer, K. S. *J. Am. Chem. Soc.* 1953, 75, 5259-5267. <sup>f</sup> Reference standard. <sup>g</sup> Benson, S. W.; Amano, A. *J. Chem. Phys.* 1962, 36, 3464-3471. <sup>h</sup> Error limits derive mainly from uncertainties in  $\Delta H_{f,300}(R'I)$  but allow a contribution of ± 1 cal deg<sup>-1</sup> mol<sup>-1</sup> for  $\Delta S_{300}^\circ$ ; errors in  $K_{300}$  are less significant. <sup>i</sup> Reference 19. <sup>j</sup> Benson, S. W.; Amano, A. *J. Chem. Phys.* 1962, 37, 197-198.

ation. Photolysis of an isooctane solution of hexa-*n*-butylditin, RI, and R'I (eq 9 and 10) led to values for  $K$  which were the same



as those obtained by the thermal route. The photolysis procedure was used at 0 °C for experiments involving methyl, since, in thermolysis experiments at 60 °C, there was some evidence that this radical was abstracting hydrogen from the solvent.

The values obtained for  $K$  are shown in Scheme I and generally represent an average obtained from five experiments. The equilibrium involving ethyl and *tert*-butyl radicals could not be established directly because of the magnitude of  $K$ , and hence cyclopentyl and *sec*-butyl radicals were used as intermediates linking these two.

The values of  $K$  measured in these experiments are solution values. However, if we assume that the free energies of mixing and vaporization of the radicals are similar to those of their parent alkanes, we can treat these values as being equivalent to gas-phase data. This is because heats of mixing of alkyl iodides and alkanes with hydrocarbons are small (<100 cal mol<sup>-1</sup>),<sup>15</sup> and since only differences in these values alter  $K$ , their effect is negligible. Moreover, corrections to the free energies of the radicals and iodides for vaporization are subject to "compensation effect"<sup>16</sup> and are also negligible. Values of  $K_{333}$  were corrected to  $K_{300}$  by using the entropies and heat capacities of the components in equilibria<sup>9a,16</sup> and are shown in Table I along with the other thermodynamic parameters used in the calculation of  $\Delta H_{f,300}(R\cdot)$  and BDE<sub>300</sub>(R-H).

The value of  $\Delta H_{f,300}(\text{Et}\cdot)$  obtained in this work is higher than the normally accepted value of 25.9 ± 1.3 kcal mol<sup>-1</sup><sup>20</sup> and leads to a value for the C-H bond dissociation energy in ethane of 100.7 ± 1.0 kcal mol<sup>-1</sup>. We note that the higher value for  $\Delta H_{f,300}(\text{Et}\cdot)$  leads to a reconciliation of currently conflicting data on the self-reaction of the ethyl radical,<sup>6,9a</sup> which enhances our confidence in the accuracy of this method.

The heat of formation for *tert*-butyl (Table I) is within experimental error of recent measurements<sup>4,6,7</sup> which cover the range

(15) Wisniak, J.; Tamir, A. *Physical Sciences Data 1*, "Mixing and Excess Thermodynamic Properties"; Elsevier: New York, 1978.

(16) Benson, S. W. "Thermochemical Kinetics"; 2nd Ed. Wiley: New York, 1976.

(17)  $\Delta H_{f,300}(R'I)^8$  were checked by measuring the heats of reaction for the reductions of the iodides by tri-*n*-butylhydride in isooctane solvent. Taking  $\Delta H_{f,300}(\text{CH}_3\text{I}) = 3.4$  kcal mol<sup>-1</sup> as a standard,  $\Delta H_{f,300}(\text{EtI})$  and  $\Delta H_{f,300}(\text{t-BuI})$  were found to be -3.3 ± 1.0 and -16.7 ± 1.0 kcal mol<sup>-1</sup>, in good agreement with the gas-phase data. Castelhan, A. L.; Marriott, P. R.; Griller, D., unpublished results.

(18) Purnell, J. H.; Quinn, C. P. *J. Chem. Soc.* 1964, 4049-4052. This data takes proper account of the out-of-plane vibrational frequencies for R'. See also: Pacansky, J.; Gardini, G. P.; Bargon, J. *J. Am. Chem. Soc.* 1976, 98, 2665-2666. Griller, D.; Marriott, P. R.; Preston, K. F. *J. Chem. Phys.* 1979, 71, 3703-3707.

(19) Lewis, R. S.; Benson, S. W. *Int. J. Chem. Kinet.*, in press. The calculation of  $S_{300}^\circ(\text{t-Bu}\cdot)$  is based upon experimentally determined values<sup>21</sup> of the vibrational frequencies of the radical. See also: Pacansky, J.; Chang, J. S. *Chem. Phys. Lett.*, in press. These authors calculate  $S_{300}^\circ(\text{t-Bu}\cdot) = 76$  cal deg<sup>-1</sup> mol<sup>-1</sup>. The difference between the two approaches rests upon assumptions about the barrier for asymmetric rotation of the methyl groups in the *tert*-butyl radical.

(20) Golden, D. M.; Benson, S. W. *Chem. Rev.* 1969, 69, 125-134.

(21) Griller, D.; Ingold, K. U.; Krusic, P. J.; Fischer, H. *J. Am. Chem. Soc.* 1978, 100, 6750-6751. Pacansky, J.; Brown, D. W.; Chang, J. S. *J. Phys. Chem.*, in press.

$\Delta H_{f,300}(\text{t-Bu}\cdot) = 8.4\text{--}10.5$  kcal mol<sup>-1</sup> and is in excellent agreement with the results of two unpublished determinations.<sup>19,22</sup> Since our value falls (albeit fortuitously) at the mean of the best available data, we recommend its use until a more accurate method of measurement becomes available. This work is being extended to measure the heats of formation of a variety of radicals.

(22) Lossing, F. P., unpublished results give  $\Delta H_{f,300}(\text{t-Bu}\cdot) = 9 \pm 1$  kcal mol<sup>-1</sup>.

(23) After this work was submitted, details of a further measurement of  $\Delta H_{f,300}(\text{t-Bu}\cdot) = 10.5 \pm 1.0$  were published. See: Canosa, C. E.; Marshall, R. M. *Int. J. Chem. Kinet.* 1981, 13, 303-316.

## <sup>29</sup>Si CP/MAS NMR Studies of Methylchlorosilane Reactions on Silica Gel

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Covalently attached bonded-phase materials prepared by the reaction of silating agents with the surface of silica gel have found important applications in many areas.<sup>1-4</sup> As part of a continuing study of such systems by <sup>29</sup>Si and <sup>13</sup>C cross-polarization and magic-angle spinning (CP/MAS) NMR<sup>5,6</sup> spectroscopy, we wish to report some preliminary observations on the reactions of a homologous series of methylchlorosilanes with a commercial silica gel (Fisher S-157). Recent CP and MAS studies of related materials have shown great promise for structure elucidation.<sup>5-8</sup>

Surface-silane reactions were carried out by exposing samples of silica gel, prepared under vacuum at 240 °C, to vapors from refluxing methylchlorosilane reagent for a period of about 12 h. The reaction temperature was maintained at 200 °C by independent heating of the sample cell and subsequently for an additional 4 h while the cell was evacuated to remove any unreacted, physically adsorbed reagent. Solid-state <sup>29</sup>Si spectra were obtained at 11.88 MHz on a JEOL FX-60QS spectrometer.<sup>9</sup>

We recently reported <sup>29</sup>Si chemical shift assignments for the three observable resonances of the silica gel surface.<sup>6</sup> These are labeled a, b, and c in Figure 1A which also shows a hypothetical surface segment suggested by the <sup>29</sup>Si data. Resonance a cor-

- (1) Gilpin, R. K.; Burke, M. F. *Anal. Chem.* 1973, 45, 1383-1389.
- (2) Leyden, D. E.; Luttrell, G. H. *Anal. Chem.* 1975, 47, 1612-1617.
- (3) Leal, L.; Anderson, D. L.; Bowman, F. B.; Burwell, R. L., Jr. *J. Am. Chem. Soc.* 1975, 97, 5125-5129.
- (4) Horvath, C.; Melander, W. *J. Chromatogr. Sci.* 1977, 15, 393-404.
- (5) Maciel, G. E.; Sindorf, D. W.; Bartuska, V. J. *J. Am. Chem. Soc.* 1980, 102, 7606-7607.
- (6) Maciel, G. E.; Sindorf, D. W. *J. Chromatogr.* 1981, 205, 438-443.
- (7) Lippmaa, E.; Magi, M.; Samoson, A.; Engelhardt, G.; Grimner, A. R. *J. Am. Chem. Soc.* 1980, 102, 4889-4893.
- (8) Slotfeldt-Ellingsen, D.; Resing, H. A. *J. Phys. Chem.* 1980, 84, 2204-2209.
- (9) All <sup>29</sup>Si CP/MAS spectra employed contact times of 10 ms and repetition times of 0.50 s. The spectra shown represent 10 000 to 60 000 repetitions. Peak intensities in the -109-ppm region are especially sensitive to the quality of the Hartmann-Hahn match<sup>10</sup> and should therefore be viewed with caution. <sup>13</sup>C CP/MAS spectra of the particular systems discussed here were found to show just one line due to (CH<sub>3</sub>Si<) carbons and were therefore not very informative. However, <sup>13</sup>C spectra of systems with more complex carbon frameworks are sometimes very useful.<sup>6,12</sup>