Reactivity Patterns of the Methyl Radical[1]

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Abstract: The relative reactivities of a series of hydrogen donors toward the methyl radical were measured in solution at 110°. Methyl radicals were generated by the thermal decomposition of *tert*-butyl peracetate in mixtures of the hydrogen donor RH and the standard substrate *tert*-butyl mercaptan-*S-d*, and the ratio $[CH_4]/[CH_3D]$ was determined by mass spectrometry: $CH_3\cdot + RH \rightarrow CH_4 + R\cdot$ (k_{RH}) and $CH_3\cdot +$ *tert*-BuSD $\rightarrow CH_3D +$ *tert*-BuS· (k_{SD}). A wide range of substrates was studied, including compounds containing alkyl, allylic, benzylic, and cycloalkyl hydrogens, and the data are combined to give a scale of rate constants for reaction of methyl radicals with any given type of hydrogen. Our scale of reactivities for *hydrogen-abstraction* reactions and Szwarc's scale[3] for *addition* reactions can be put on a common basis using the reactivity of isooctane as the bridge: $CH_3\cdot +$ (olefinic or aromatic compound) $\rightarrow CH_3\text{–}C\text{–}C\cdot$ (k_{add}) and $CH_3\cdot + C_8H_{18} \rightarrow CH_4 + C_8H_{17}\cdot$ (k_{iso}). This permits us to tabulate the relative reactivity toward methyl radicals of virtually every type of hydrocarbon—saturated, olefinic, or aromatic; from these data the relative reactivity of any hydrocarbon of interest can be predicted. The selectivity of the methyl radical toward various types of hydrogens is compared with that of a number of other radicals. The methyl radical is found to be quite similar to the phenyl radical in selectivity. Calculations show the relative reactivity of a series of donors toward the methyl radical is the same in the gas phase and in solution.

The methyl radical has played a key role in the history of free radical chemistry. In 1929–1930, Paneth[4] convincingly demonstrated for the first time the existence of a radical in the gas phase using tetramethyllead and similar compounds. Since then, significant quantitative information has resulted from intensive research on several types of methyl radical reactions. Recent compilations[5] show that more quantitative gas-phase kinetic data are known for the methyl radical than for any other free radical. In contrast, the data available for the liquid phase are less complete. In 1950, Edwards and Mayo[6] published a study of the liquid-phase reactions of methyl radicals, but they were able to study only eight solvents. Recently, we[7] extended these data and, in addition, pointed out a limitation of the Edwards and Mayo system.

In 1956–1958, Szwarc, *et al.*,[3,8,9] reported data for abstraction of allylic hydrogens employing a kinetic scheme developed by Buckley, Leavitt, and Szwarc.[9] Szwarc's results led him to conclude that the H abstraction from olefins only involves the hydrogen atoms α to the double bond. Subsequent research suggests that this conclusion is erroneous. For instance, in their study of the phenyl radical, Bridger and Russell[10] reported that 25% of the reactivity of 1-pentene is due to alkyl hydrogens which are not α to the double bond. Likewise, the reported reactivities of both the methyl and the *p*-nitrophenyl[11] radicals do not support Szwarc's conclusion. In addition, the method of Szwarc, *et al.*,[9] required calculating the reactivity by the use of the product of an experimentally determined slope and an intercept, and this reduces the accuracy of the method.

In 1962, Berezin and Dobish[12] used tritiated solvents as standard substrates and investigated the selectivity of the methyl radical. Their results gave relative reactivities for primary, secondary, and tertiary hydrogens of 1:10:66–179. The utility of their data is of limited value, however, because they chose a restricted set of compounds. They used only *n*-heptane, *cis*- and *trans*-decalin, and cyclohexane as model compounds to determine relative reactivities, and this is not adequate.[13] For example, Bridger and Russell[10] studied five normal alkanes and three monomethylalkanes to determine relative reactivities of the phenyl radical.

A 1956 study by Szwarc[9] reports the methyl radical selectivity toward primary, secondary, and tertiary benzylic hydrogens to be 1:4.1:12.9, and a more recent study in these laboratories[7] is in excellent agreement. At the same time, we[7] also reported the Hammett correlation for the reaction with substituted toluenes. The methyl radical was found to be very slightly electrophilic; the Hammett equation gave a ρ^+ of approximately -0.1.[14]

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(3) M. Szwarc and J. H. Binks, "Theoretical Organic Chemistry," Kekule Symposium, 1958, Butterworths, London, 1958, p 262.

(4) F. Paneth and W. Hofeditz, *Ber.*, **62**, 1335 (1929).

(5) (a) A. F. Trotman-Dickenson, *Advan. Free-Radical Chem.*, **1**, 1 (1965); (b) A. F. Trotman-Dickenson and G. S. Milne, "Tables of Bimolecular Gas Reactions," National Standard Reference Data Series, National Bureau of Standards, No. 9, U. S. Government Printing Office, Washington, D. C., 1967.

(6) F. G. Edwards and F. R. Mayo, *J. Amer. Chem. Soc.*, **72**, 1265 (1950).

(7) W. A. Pryor, U. Tonellato, D. L. Fuller, and S. Jumonville, *J. Org. Chem.*, **34**, 2018 (1969). We have redetermined the reactivity of chloroform as a hydrogen donor and have been unable to duplicate our earlier results. For a reason we do not understand at present, chloroform appears to be an anomalous solvent using the Edwards and Mayo technique.

(8) R. P. Buckely and M. Szwarc, *Proc. Roy. Soc., Ser. A*, **240**, 396 (1957).

(9) R. P. Buckley, F. Leavitt, and M. Szwarc, *J. Amer. Chem. Soc.*, **78**, 5557 (1956).

(10) R. F. Bridger and G. A. Russell, *ibid.*, **85**, 3754 (1963).

(11) W. A. Pryor, K. Smith, J. Echols, and D. L. Fuller, *J. Org. Chem.*, in press.

(12) (a) V. L. Antonovskii, I. V. Berezin, and L. V. Shevel'kova, *Proc. Acad. Sci. USSR*, **134**, 887 (1960); (b) I. V. Berezin and O. Dobish, *ibid.*, **142**, 1 (1962); (c) *ibid.*, **144**, 382 (1962).

(13) The necessity of using as many compounds as possible can be seen from the following example using our own data. If only hexane and hexadecane are used to calculate the selectivity of the methyl radical toward primary and secondary alkyl–hydrogen bonds, a ratio of 1:3.9 is obtained. If the relative reactivity of hexadecane is increased by only 5%, this primary to secondary ratio changes to 1:95. However, if six normal alkanes are used, a 5% increase in the value for hexadecane changes the primary to secondary reactivity ratio from 1:4.3 to only 1:5.7.

Thus, there are only limited and inadequate data available for hydrogen atom abstraction in solution by the methyl radical. We here report extensive new data determined using a new experimental procedure. In addition, we have been able to overlap the reactivity scales of hydrogen-abstraction and addition reactions for the methyl radical, allowing the calculation of the total reactivity of saturated, olefinic, or aromatic hydrocarbons.

Kinetic Scheme. The thermal decomposition of *tert*-butyl peracetate, *tert*-BPA, was used as the source of methyl radicals. This initiator undergoes initial cleavage at the O–O bond followed by scission of the C–C bond.[15]

$$CH_3CO_3C(CH_3)_3 \xrightarrow{k_1} CH_3CO_2\cdot + \cdot OC(CH_3)_3 \qquad (1)$$

$$CH_3CO_2\cdot \xrightarrow{k_2} CH_3\cdot + CO_2 \qquad (2)$$

The methyl radicals were generated in a mixture of *tert*-BPA, a hydrogen donor (RH), and *tert*-butyl mercaptan-*S*-*d* (*tert*-BuSD). Methyl radicals which escape the cage and become free may abstract a hydrogen atom from either RH or *tert*-BuSH (present as an impurity) or abstract a deuterium atom from *tert*-BuSD.

$$CH_3\cdot + RH \xrightarrow{k_{RH}} CH_4 + R\cdot \qquad (3)$$

$$CH_3\cdot + \textit{tert}\text{-BuSD} \xrightarrow{k_{SD}} CH_3D + \textit{tert}\text{-BuS}\cdot \qquad (4)$$

$$CH_3\cdot + \textit{tert}\text{-BuSH} \xrightarrow{k_{SH}} CH_4 + \textit{tert}\text{-BuS}\cdot \qquad (5)$$

Steady-state kinetic analysis of this scheme gives the following equation

$$\frac{[CH_4]}{[CH_3D]} = \frac{k_{RH}}{k_{SD}}\frac{[RH]}{[\textit{tert}\text{-BuSD}]} + \frac{k_{SH}[\textit{tert}\text{-BuSH}]}{k_{SD}[\textit{tert}\text{-BuSD}]} \qquad (6)$$

A plot of $[CH_4]/[CH_3D]$ *vs.* [RH]/[*tert*-BuSD] should yield a straight line with a slope of k_{RH}/k_{SD} and an intercept of k_{SH}/k_{SD} [*tert*-BuSH]/[*tert*-BuSD]. Some CH_4 may also be formed *via* attack on the methyl groups of *tert*-BuSD, but its formation does not affect the measured slope k_{RH}/k_{SD}.

Controls. Several assumptions are implicit in eq 6. The rate laws must be first order in $CH_3\cdot$, *tert*-BuSD, and RH; *i.e.*, reactions 3 and 4 must be elementary processes. To test the assumption the initial perester concentration was varied; if reactions 3 and 4 are not of the same kinetic order in the methyl radical, or if other reactions occur, a change in *tert*-BPA initial concentration will lead to a systematic change in the $[CH_4]/[CH_3D]$ ratio. Table I (column 1, experiments 11–15) shows the ratio to be constant below approximately 0.1 *M tert*-BPA. The standard concentration of perester in our studies was chosen to be 0.05 *M*.

Table I. Products from the Thermolysis of *tert*-Butyl Peracetate in Octane–*tert*-Butyl Mercaptan-*S*-*d* at 110°

Expt	$[C_8H_{18}]$/[*tert*-BuSD]	Initial [*tert*-BPA], *M*	*tert*-BPA remaining, %	$[CH_4]/[CH_3D]$
1	10.7	0.05	80	0.70
2	10.7	0.05	60	0.72
3	10.7	0.05	34	0.63
4	10.7	0.05	25	0.62
5	10.7	0.05	18	0.75
6	10.7	0.05	12.5	0.67
7	10.7	0.05	0.135	0.68
8	8.6	0.5	12.5	1.3
9	8.6	0.25	12.5	1.1
10	8.6	0.17	12.5	0.8
11	8.6	0.071	12.5	0.62
12	8.6	0.050	50.0	0.59
13	8.6	0.038	12.5	0.58
14	8.6	0.021	12.5	0.58
15	8.6	0.009	12.5	0.56

Of equal significance, we measured the $[CH_4]/[CH_3D]$ ratio as a function of the amount of the *tert*-BPA decomposed. Table I (experiments 1–7) shows that the $[CH_4]/[CH_3D]$ ratios remain relatively constant. If reactions 7 and 8 occurred to a significant extent, these ratios would not have remained constant at higher extents of decomposition.

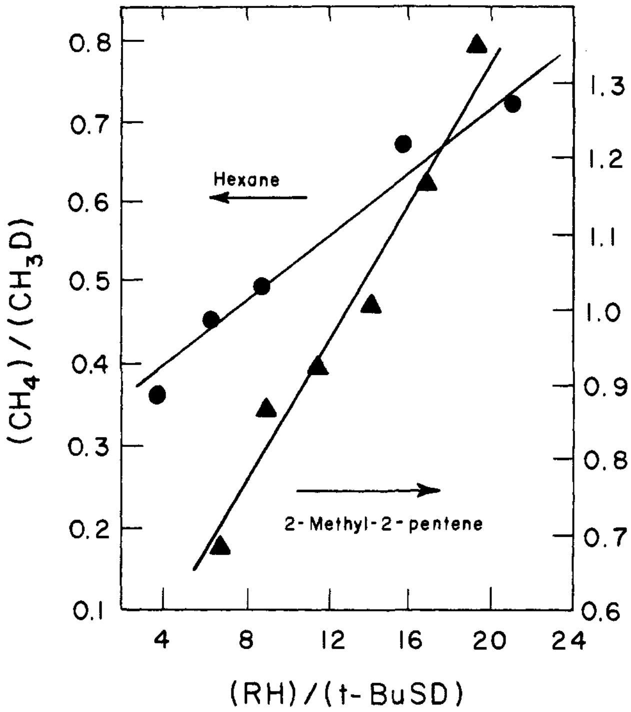

Figure 1. A typical plot of eq 6 for hydrogen atom abstraction by the methyl radical from hexane and 2-methyl-2-pentene.

$$\textit{tert}\text{-BuSD} + R\cdot \longrightarrow RD + \textit{tert}\text{-BuS}\cdot \qquad (7)$$

$$\textit{tert}\text{-BuS}\cdot + RH \longrightarrow R\cdot + \textit{tert}\text{-BuSH} \qquad (8)$$

Experimental Section

Chemicals. Alkanes purchased from Phillips Petroleum Co. and Columbia Organic Chemicals Co. were purified using the method of

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(14) Minisci, *et al.*, have interpreted their data on homolytic substitution of pyridinium salts as an indication that the methyl radical is quite nucleophilic: G. P. Gardini, F. Minisci, and G. Palla, private communication. However, their system (2.5 *M* H_2SO_4) is considerably different from previous systems studied.[7] It should also be pointed out that abstraction from toluenes by the methyl radical is quite exothermic and for this reason will show reduced polar character; see G. A. Russell, *J. Org. Chem.*, **23**, 1407 (1958), and C. Ruchardt, *Angew. Chem., Int. Ed. Engl.*, **9**, 830 (1970). Nevertheless, the Hammett correlation is the classical method for probing the polar nature of any reactive species, and it has been applied to many free radicals; see J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **41**, 1744 (1963).

(15) (a) W. A. Pryor and K. Smith, *J. Amer. Chem. Soc.*, **92**, 5403 (1970); (b) T. Koenig, J. Huntington, and R. Cruthoff, *ibid.*, **92**, 5413 (1970). (c) The yield of methyl radicals from *tert*-butoxy radicals will be small at the temperature used here and in the presence of thiol. However, even if methyl radicals were produced from a source other than eq 1 and 2, the kinetic analysis would not be affected.

Table II. Selectivity of the Methyl Radical in Hydrogen Abstraction Reactions from Various Hydrocarbons at 110°

Compound	$k_{RH}/k_{SD} \times 10^2$ [a]	Intercept[a]	Relative k_{RH}	
			Obsd	Calcd[b]
Hexane	2.07 ± 0.23	0.31	1.00 ± 0.16	1.09
Octane	3.09 ± 0.29	0.37	1.49 ± 0.21	1.54
Decane	4.06 ± 0.35	0.22	1.95 ± 0.27	2.00
Dodecane	5.17 ± 0.35	0.34	2.49 ± 0.32	2.46
Tetradecane	6.12 ± 0.40	0.43	2.96 ± 0.38	2.92
Hexadecane	6.96 ± 0.40	0.35	3.35 ± 0.42	3.38
3-Methylhexane	4.38 ± 0.31	0.20	2.17 ± 0.28	2.17
2-Methylpentane	3.79 ± 0.10	0.23	1.83 ± 0.21	1.94
2,3-Dimethylbutane	6.22 ± 0.29	0.06	2.99 ± 0.36	2.79
2,4-Dimethylpentane	3.41 ± 0.08	0.15	1.65 ± 0.19	3.02[c]
2,3-Dimethylpentane	3.86 ± 0.50	0.12	1.86 ± 0.32	3.02[c]
2,2,4-Trimethylpentane	2.21 ± 0.17	0.20	1.06 ± 0.14	1.89[c]
Cyclopentane	2.11 ± 0.21	0.19	1.02 ± 0.15	
Cyclohexane	2.09 ± 0.08	0.16	1.01 ± 0.12	
Cycloheptane	3.64 ± 0.11	0.15	1.75 ± 0.20	
Cyclooctane	7.25 ± 0.29	0.09	3.50 ± 0.35	
Toluene	1.64 ± 0.10	0.46	0.79 ± 0.10	
Ethylbenzene	4.74 ± 0.42	0.24	2.28 ± 0.32	
Cumene	7.64 ± 0.13	0.32	3.58 ± 0.41	
p-Xylene	3.65 ± 0.44	0.25	1.75 ± 0.29	
1-Hexene	3.45 ± 0.07	0.24	1.67 ± 0.19	1.68
1-Octene	3.59 ± 0.34	0.31	1.73 ± 0.29	2.12
1-Decene	6.12 ± 0.19	0.26	2.96 ± 0.29	2.55
2-Octene	5.42 ± 0.48	0.31	2.61 ± 0.37	2.63
trans-3-Hexene	4.02 ± 0.23	0.39	1.94 ± 0.24	2.47
2-Methyl-1-pentene	5.14 ± 0.31	0.38	2.48 ± 0.31	2.18
2-Methyl-2-pentene	4.21 ± 0.28	0.32	2.03 ± 0.26	2.67
Cyclohexene	2.87 ± 0.16	0.34	1.38 ± 0.17	
Methyl acetate	4.02 ± 0.15	0.17	1.94 ± 0.23	
Anisole	2.97 ± 0.16	0.25	1.43 ± 0.18	
Phenetole	3.40 ± 0.44	0.28	1.64 ± 0.28	
3-Methyl-1-hexene	4.97 ± 0.33	0.37	2.40 ± 0.31	2.60
Dioxane	4.88 ± 0.46	0.10	2.35 ± 0.34	
Diisopropyl ether	23.2 ± 0.91	0.05	11.2 ± 1.32	
Diethyl ether	17.9 ± 1.81	0.24	8.65 ± 1.13	

[a] The values were determined using a least-squares analysis of eq 6. The standard deviation of the slope is given. The average value of the intercept is 0.26. Deviation from this number arises from the use of thiol with different per cent deuteration, as well as experimental error. [b] Calculated using eq 9 (see text). [c] The observed reactivities of these compounds are abnormally low and were not used in obtaining calculated reactivities; see text.

Murray and Keller.[16] Alkenes were purified by passing them through a column packed with alumina W200 basic. Aromatic compounds were stirred for several hours with concentrated sulfuric acid, washed with 10% sodium bicarbonate and with distilled water, dried, distilled, stored over nitrogen, and passed through a column packed with an alumina W200 basic prior to use. Ethers were purified by the method suggested by Wiberg.[17] *tert*-Butyl peracetate purchased from Lucidol was purified by distillation at room temperature and 1 Torr. *tert*-Butyl mercaptan-*S*-*d* was prepared by stirring the thiol with D_2O until the nmr spectrum of the thiol showed it to be approximately 98% deuterated. The thiol was dried and distilled. Monodeuteriomethane was prepared as described by Turkevich, Friedman, Solomon, and Wrightson.[18] Mass spectral analysis showed only trace amounts of air present. Ultra-high purity methane (99.97%) was purchased from Matheson Gas Products. Deuterium oxide (99.8% deuterium) was purchased from International Chemical and Nuclear Corp.

Procedure of Kinetic Runs. The reaction mixtures were prepared by mixing 0.05 *M tert*-BPA in RH with 0.05 *M tert*-BPA in a mixture of RH and *tert*-BuSD having an approximate [RH]/[*tert*-BuSD] ratio of 5. The reaction mixtures were then transferred to 9-mm o.d. Pyrex samples tubes which were tapered at the closed end. Ampoules were degassed by the standard procedure[19] and sealed under vacuum. The samples were allowed to decompose in a constant-temperature bath (110°) for one half-life (181.9 min).[20]

Analytical Technique. The samples were analyzed on a CEC Model 61–620 mass spectrometer by a procedure similar to that used by Gifford, Rock, and Comaford.[21] The mass spectral data were obtained from the mass patterns of the pure compounds for both methane and methane-*d*.

Figure 1 shows a typical set of kinetic data plotted for eq 6. Table II summarizes the relative rate constants for the series of hydrogen donor compounds studied in this laboratory. Decomposition of *tert*-BPA in toluene and *tert*-BuSD gave a relative reactivity of 1.84 (hexane = 1). The value appears too large; however, a reactivity of 0.79 was obtained when toluene was saturated with D_2O. In contrast to toluene, cumene gave the same reactivity when either saturated with D_2O or dried by passing through a column packed with activated alumina. The variation in the values obtained for toluene may be related to its low relative reactivity.

Discussion

Reactivities of Alkanes. The results of the least-squares analysis of eq 6 are given in Table II. The reactivities of the primary, secondary, and tertiary carbon–hydrogen bonds were determined using simultaneous equations for the normal alkanes which led to 12 combinations of two equations in two unknowns. Averaging the results gave 0.0269 and 0.117 for the reactivity of primary and secondary carbon–hydrogen bonds. The reactivity of the tertiary carbon–hydrogen bond was then calculated using the above values and the

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[20] P. D. Bartlett and R. R. Hiatt, *ibid.*, **80**, 1398 (1958).

[21] A. P. Gifford, S. M. Rock, and D. J. Comaford, *Anal. Chem.*, 21, 1062 (1949).

Table III. Relative Rate Constants for the Reaction of Various Radicals with Alkyl Hydrogens (per Hydrogen)[dd]

$$RH + X\cdot \longrightarrow XH + R\cdot$$

Radical	Phase[a]	Temp, °C	No. of compd used	Type of hydrogen			Ref
				Primary	Secondary	Tertiary	
F	g	25	4[b]	1	1.2	1.4	*o*
Cl	g	25	5[c]	1	4.6	6	*p*
Br	g	98		1	250	6300	*q*
CF_3	g	182	3[d]	1	7.8	24	*r*
CCl_3	g	190	3[e]	1	80	2300	*s*
CH_3O	g	250	5[c]	1	8	27	*t*
CH_3	g	182	9[j]	1	7	50	*u*
HO	g	17.5	3[f]	1	5.4	9.9	*v*
tert-BuO	l	40	2[g]	1	10	44	*w*
C_6H_5	l	60	10[h]	1	9.3	44	*x*
p-$O_2NC_6H_4$	l	60	9[i]	1	11	49	*y*
Cl	l	40	2[k]	1	3.7	4.7	*z*
CH_3	l	110	10[l]	1	4.3	46	*aa*
H	l	35	6[m]	1	5	40	*bb*
n-C_6H_{13}	l	74	3[n]	1	3.6	41	*cc*

[a] g and l represent the gas and liquid phase, respectively. [b] Propane, butane, isobutane, and neopentane. [c] Ethane, neopentene, propane, butane, and isobutane. [d] Ethane, propane, and 2,3-dimethylbutane. [e] Propane, butane, and isobutane. [f] Ethane, propane, and isobutane. [g] Butane and 2,3-dimethylbutane. [h] Pentane, hexane, heptane, octane, hexadecane, 3-methylpentane, 2-methylpentane, 3-methylhexane, dimethylpropane, and tetramethylbutane. [i] Tetramethylbutane, hexane, heptane, octane, decane, 2-methylpentane, 3-methylpentane, 2-methylhexane, and 3-methylhexane. [j] Ethane, dimethylpropane, tetramethylbutane, butane, pentane, hexane, 2-methylpropane, 2,3-dimethylbutane, and 2,3,4-trimethylpentane. [k] Pentane and 2,3-dimethylbutane. [l] Hexane, octane, decane, dodecane, tetradecane, hexadecane, 3-methylhexane, 2-methylpentane, and 2,3-dimethylbutane. [m] Hexane, dodecane, cyclohexane, cyclopentane, 2,3-dimethylbutane, and 2,5-dimethylhexane. [n] *tert*-Butyl alcohol, cyclohexane, and 2,3-dimethylbutane. [o] G. C. Fettis, J. H. Knox, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1064 (1960). [p] J. H. Knox and R. L. Nelson, *Trans. Faraday Soc.*, **55,** 937 (1959). [q] A. F. Trotman-Dickenson, *Advan. Free-Radical Chem.*, **1,** 1 (1965). [r] G. O. Pritchard, H. O. Pritchard, H. I. Schiff, and A. F. Trotman-Dickenson, *Trans. Faraday Soc.*, **52,** 849 (1956). [s] B. P. McGrath and J. M. Tedder, *Bull. Soc. Belg.*, **71,** 772 (1962). [t] R. Shaw and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 3210 (1960). [u] A. F. Trotman-Dickenson, "Gas Kinetics," Butterworths, London, 1955. [v] T. Be'rces and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 4281 (1961). [w] C. Walling and B. B. Jacknow, *J. Amer. Chem. Soc.*, **82,** 6108 (1960). [x] R. F. Bridger and G. A. Russell, *ibid.*, **85,** 3754 (1963). [y] W. A. Pryor, K. Smith, J. Echols, and D. Fuller, *J. Org. Chem.*, in press. [z] G. A. Russell, *J. Amer. Chem. Soc.*, **80,** 4997 (1958). [aa] Present work. [bb] W. A. Pryor and J. P. Stanley, *J. Amer. Chem. Soc.*, **93,** 1412 (1971). [cc] D. F. DeTar and D. V. Wells, *ibid.*, **82,** 5839 (1960). [dd] Data have been rounded to two significant figures; see text.

data for two monomethylalkanes and 2,3-dimethylbutane. The average of these three values was 1.24. Normalization gives a relative reactivity series of 1:4.3:46 for primary, secondary, and tertiary aliphatic hydrogens. The total reactivity of any aliphatic compound can be calculated from eq 9. Re-

$$\text{rel } k_H(\text{calcd}) = (\text{no. of primary H's})(0.0269) + (\text{no. of secondary H's})(0.117) + (\text{no. of tertiary H's})(1.24) \quad (9)$$

activities calculated using this equation are shown in Table II and are in excellent agreement with the observed value for most compounds. However, observed reactivities are only about one-half the calculated reactivities for alkanes possessing a 2,4-dimethyl arrangement. This low reactivity for 2,4-dimethylalkanes has been observed both by Bridger and Russell[10] and by Pryor and Stanley.[22] It apparently is related to the conformation of the alkane rather than the size of the radical since H atoms and methyl, phenyl, and *p*-nitrophenyl radicals all give a similar discrepancy between observed and calculated values for these compounds. These compounds were omitted from calculations of average reactivities of hydrogens.

As can be seen from the data in Table II, the standard deviations in the relative k_H values are 10–15%. This reproducibility is typical of the precision, and probably of the accuracy, of this type of study. Therefore, both our data and literature values in Tables III–IX should be considered as accurate to only 10–20%, and the values in Tables III–IX have been rounded off to two figures although this introduces rounding errors in some cases.

Table III compares the relative reactivities of a series of radicals toward alkyl hydrogens. Column 4 shows the number of compounds employed by various workers in determining relative reactivities; for example, the calculations on HO· utilized three compounds whereas those for $C_6H_5\cdot$ utilized ten. As pointed out above, the derived relative reactivities are not reliable when a small number of compounds is used. In addition, these relative reactivities were determined at different temperatures and only qualitative comparisons can be made.

An examination of Table III shows that radicals can be divided into three classes: unselective (*e.g.*, fluorine and, to a lesser extent, chlorine atoms); selective (*e.g.*, Br· and ·CCl_3); and intermediate radicals. The data may indicate some difference in selectivity for the methyl radical and chlorine atom in the gas and liquid phases. The selectivities of the hydrogen atom and the methyl and *n*-hexyl radicals are approximately the same.

Reactivities of Cycloalkanes. Cyclopentane, cyclohexane, cycloheptane, and cyclooctane give relative reactivities *per hydrogen* in the order: $C_6 < C_5 < C_7 < C_8$. Table IV shows similar data for five different radicals and two facts become evident: first, all the radicals exhibit the same trend in reactivity; and, second, of the five radicals, $CCl_3\cdot$ is the most selective, Cl· is the least selective, and methyl, phenyl, and *p*-nitrophenyl are of nearly equal selectivity. This is the same selectivity pattern observed for acyclic donors. The data in Table IV indicate that I-strain[23]

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(22) W. A. Pryor and J. P. Stanley, *J. Amer. Chem. Soc.*, **93,** 1412 (1971).

Table IV. Relative Rate Constants for the Reaction of Various Radicals with Cycloalkanes (per Hydrogen)

Cycloalkanes, ring size	$CH_3\cdot$[a] (110°)	$C_6H_5\cdot$[b] (60°)	$NO_2C_6H_4\cdot$[c] (60°)	$CCl_3\cdot$[d] (80°)	$Cl\cdot$[d] (40°)	$Cl\cdot$ in CS_2[d] (40°)
5	1.2	1.2	1.2	1.6	1.0	1.2
6	(1)	(1)	(1)	(1)	(1)	(1)
7	1.5	1.8	1.9	3.3	1.0	2.0
8	2.2	2.0	2.1	9.2	1.5	3.8

[a] Present work. [b] R. F. Bridger and G. A. Russell, *J. Amer. Chem. Soc.*, **85,** 3754 (1963). [c] W. A. Pryor, K. Smith, J. Echols, and D. Fuller, *J. Org. Chem.*, in press. [d] E. S. Huyser, H. Schimke, and R. L. Burham, *J. Org. Chem.*, **28,** 2141 (1963). [e] Data have been rounded to two significant figures; see text.

Table V. Relative Rate Constants for the Reaction of Various Radicals with Benzylic Hydrogens[f]

$$RH + X\cdot \longrightarrow X\text{-}H + R\cdot$$

Radical	Temp, °C	Benzylic C–H bonds: Primary	Benzylic C–H bonds: Secondary	Benzylic C–H bonds: Tertiary	Ref
Methyl	110	1	4.2	13	*a*
Phenyl	60	1	4.6	9.7	*b*
p-Nitrophenyl	60	1	4.7	22	*c*
tert-Butoxy	40	1	3.2	6.8	*d*
Bromine	40	1	20	40	*e*
Trichloromethyl	40	1	50	260	*e*

[a] Present work. [b] R. F. Bridger and G. A. Russell. *J. Amer. Chem. Soc.*, **85,** 3754 (1963). [c] W. A. Pryor, K. Smith, J. Echols, and D. Fuller, *J. Org. Chem.*, in press. [d] C. Walling and W. Thaler, *J. Amer. Chem. Soc.*, **83,** 3877 (1961). [e] G. A. Russell and C. DeBoer, *ibid.*, **85**, 3136 (1963). [f] Data have been rounded to two significant figures; see text.

Table VI. Relative Rate Constants for Reaction of Various Carbon–Hydrogen Bonds toward Common Radicals and Atoms[g]

Type of bond	Methyl[a] 110°(l)	Methyl[b] 182°(g)	Phenyl[c] 60°(l)	Nitrophenyl[d] 60°(l)	*tert*-Butoxy[e] 40°(l)	Chlorine[f] 40°(l)
Primary alkyl	(1)	(1)	(1)	(1)	(1)	(1)
Secondary alkyl	4.3	7	9.3	11	12	3.7
Tertiary alkyl	46	50	44	49	44	4.5
Primary allylic	9		15	17	20	
Secondary allylic	21		30	35	93	
Tertiary allylic	66		120		180	
Primary benzylic	10		9.1	5.9	10	1.3
Secondary benzylic	41		42	36	32	3.1
Tertiary benzylic	130		88	130	69	6.9
Cyclopentane	3.8		10	12	14	2.6
Cyclohexane	3.1		9.1	10	15	2.5
Cycloheptane	4.6		17	17		2.8
Cyclooctane	8.1		18	27		4.0
Cyclohexene (α)	11		100	91	370	

[a] Present work. [b] A. F. Trotman-Dickenson, "Gas Kinetics," Butterworths, London, 1955, p 225. [c] R. F. Bridger and G. A. Russell, *J. Amer. Chem. Soc.*, **85,** 3754 (1963). [d] W. A. Pryor, K. Smith, J. Echols, and D. Fuller, *J. Org. Chem.*, in press. [e] C. Walling and W. Thaler, *J. Amer. Chem. Soc.*, **83,** 3877 (1961). [f] G. A. Russell, *ibid.*, **80,** 4987, 5002 (1958). [g] Data have been rounded to two significant figures; see text. The symbols (g) and (l) refer to gas and liquid phase, respectively.

contributes to the reactivity of cycloalkanes in homolytic reactions.

Reactivities of Alkenes. Table II (column 5) gives the calculated reactivities of the hydrogens in alkenes relative to hexane. We obtained these values by using: average bond reactivities of 0.24, 0.553, and 1.77 for the primary, secondary, and tertiary allylic hydrogens, respectively; the values for the alkyl hydrogens as given previously; and zero reactivity for vinyl hydrogens.

Reactivities of Arenes. The determination of the relative reactivities of benzylic hydrogen atoms allows the comparison of our values with those of other workers. Table II gives relative reactivities as 1:4.2:12.9 for the primary, secondary, and tertiary benzylic hydrogen atoms, respectively, assuming nonbenzylic hydrogens to possess the reactivities of equivalently substituted alkyl hydrogens. These results are in agreement with the work of Szwarc, *et al.*,[24] and Pryor, *et al.*,[7] who reported 1:4.1:12.9 and 1:3.9:12.9, respectively.

Table V gives values of reactivities of benzylic hydrogens for several radicals. The methyl radical is similar to the phenyl radical in selectivity,[10] and is more selective than the chlorine atom[25] or *tert*-butoxy radical,[26] and less selective than the bromine atom[27] or the trichloromethyl radical.[27]

Comparison with Other Radicals. Table VI summarizes the selectivity of the methyl radical in comparison with other radicals. The methyl radical shows a selectivity pattern similar to the patterns of both the phenyl and *p*-nitrophenyl radicals.

A Unified Hydrogen Abstraction and Addition Relative Reactivity Scale. Abstraction and addition reactions of free radicals often compete; for example, the methyl radical adds to and abstracts a hydrogen from *cis*-2-butene at nearly the same rate.[28,29] Szwarc[3] has developed an extensive scale of addition rates for

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(23) H. C. Brown, *J. Chem. Soc.*, 1248 (1956).

(24) J. A. Meyer, V. Stannet, and M. Szwarc, *J. Amer. Chem. Soc.*, **83,** 25 (1961).

(25) G. A. Russell, A. Ito, and D. G. Hendry, *ibid.*, **85,** 2976 (1963).

(26) C. Walling and W. Thaler, *ibid.*, **83,** 3877 (1961).

(27) G. A. Russell and C. DeBoer, *ibid.*, **85,** 3136 (1963).

(28) N. Yokoyama and R. K. Brinton, *Can. J. Chem.*, **47,** 2987 (1969).

(29) R. J. Cvetanović and R. S. Irwin, *J. Chem. Phys.*, **46,** 1694 (1967).

methyl radicals, and we now have a scale for hydrogen abstraction. Clearly, it is desirable to put these two scales on the same basis, and this can be done using the reactivity of isooctane as the bridge.

Szwarc reported the reactivity of various unsaturated compounds using hydrogen abstraction from isooctane as the standard.[3] We have reviewed these data and have put them into a single scale which includes both olefins and aromatics[30]

$$\mathrm{CH_3\cdot} + \text{(olefinic or aromatic compound)} \xrightarrow{k_{\mathrm{add}}} \mathrm{CH_3\text{–}C\text{–}C\cdot}$$

$$\mathrm{CH_3\cdot} + \mathrm{C_8H_{18}} \xrightarrow{k_{\mathrm{iso}}} \mathrm{CH_4} + \mathrm{C_8H_{17}\cdot}$$

The reactivity of this series of unsaturated compounds relative to abstraction from *tert*-BuSD can be calculated by combining Szwarc's data and our values of $k_{\mathrm{iso}}/k_{\mathrm{SD}}$ and $k_{\mathrm{SD}}/k_{\mathrm{hexane}}$ from Table II. Table VII illustrates the method.

Table VII. Rate Constants for Addition of Methyl Radicals to Unsaturated Compounds Relative to Atom Abstraction from Various Standard Substrates, 65–110°[h]

Compound	$k_{\mathrm{add}}/k_{\mathrm{iso}}$[a]	$k_{\mathrm{add}}/k_{\mathrm{SD}}$[b]	$k_{\mathrm{add}}/k_{\mathrm{hexane}}$[c]	Rel reactivities[d]
Ethylene	26	0.57	28	480[e]
Isobutene	36	0.80	38	1,400[f]
cis-2-Butene	3	0.066	3.2	59[e]
Styrene	800	17	850	32,000[f]
Ethyl fumarate	2000	44	2100	4,000[e]
1,3-Butadiene	2000	45	2200	41,000[e]
Benzene	0.36	0.0079	0.39	2.4[g]

[a] W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966, pp 221–226. [b] $[k_{\mathrm{add}}/k_{\mathrm{iso}}][k_{\mathrm{iso}}/k_{\mathrm{SD}}]$. [c] $[k_{\mathrm{add}}/k_{\mathrm{SD}}][k_{\mathrm{SD}}/k_{\mathrm{hexane}}]$. [d] All values are relative to the primary alkyl hydrogen (1). [e] $[k_{\mathrm{add}}/k_{\mathrm{hexane}}]/2$. [f] $[k_{\mathrm{add}}/k_{\mathrm{SD}}]/1$. It was assumed that only the most stable radical would be formed: M. Miyoshi and R. K. Brinton (*J. Chem. Phys.*, **36**, 3019 (1962)) reported that when methyl radicals add to propene, the more stable radical was formed in 90% yield. [g] $[k_{\mathrm{add}}/k_{\mathrm{SD}}]/6$. [h] Data have been rounded to two significant figures; see text.

Table VIII. Relative Reactivities of Various Bonds toward the Methyl Radical at 65–110°

Type of bond	Rel reactivity[e]
Primary aliphatic	(1)
Secondary aliphatic	4.3
Tertiary aliphatic	46
Primary allylic	9
Secondary allylic	21
Tertiary allylic	66
Primary benzylic	9.1
Secondary benzylic	41
Tertiary benzylic	127
Ethylene[a]	480
Alkyl substituents	
Monosubstituted[b]	870
Unsym-disubstituted[b]	1,400
Sym-disubstituted[a]	
Cis	59
Trans	140
Trisubstituted[b]	240
Aryl substituents	
Monosubstituted[b]	32,000
Unsym-disubstituted[b]	60,000
Sym-disubstituted[a]	
Cis	570
Trans	2,100
Trisubstituted[b]	1,900
Tetrasubstituted[a]	160
Carbethoxy	
Monosubstituted[a]	36,000
Sym-disubstituted[a]	
Cis	6,600
Trans	40,000
Ethenyl substituents	
Monosubstituted[a]	41,000
Aromatic	
Benzene[c]	2.4
Naphthalene[d] (α position)	67
Anthracene[a] (9,10 position)	16,000
Pyridine[a] (β position)	18

Statistical corrections are as follows: [a] $k_{\mathrm{add}}/k_{\mathrm{iso}}$ divided by 2. [b] $k_{\mathrm{add}}/k_{\mathrm{iso}}$ divided by 1. It was assumed that only the most stable radical would be formed: M. Miyoshi and R. K. Brinton, *J. Chem. Phys.*, **36**, 3019 (1962). [c] $k_{\mathrm{add}}/k_{\mathrm{iso}}$ divided by 6. [d] $k_{\mathrm{add}}/k_{\mathrm{iso}}$ divided by 4. [e] Relative reactivities have been rounded to two significant figures; see text.

Table VIII combines both Szwarc's and our data into a single unified scale for reactivities toward the methyl radical. These data allow the calculation of the *total relative reactivity* of any two hydrocarbons toward the methyl radical, or of the relative reactivity of two reaction sites in the same molecule, even if the sites react differently. For example, from Table VIII the ratio of addition to hydrogen abstraction for *cis*-2-butene is (59 × 2)/(9 × 6) = 2.2. (The statistical corrections are for the two similar reactive ends of the double bond and the six equivalent primary allylic hydrogens.) This value is in rough agreement[31] with that obtained by Cvetanović[29] (0.8) and Brinton[28] (3.7). One note is necessary on this combined scale. Szwarc determined the reactivity of unsaturated compounds at 65°, whereas we used 110° for our hydrogen abstraction scale.[30b] However, the activation energies for addition and hydrogen abstraction are both small and are fairly similar,[29] and the variation in the ratio of addition to abstraction is small over the 45° difference in these scales.[29]

The data given in Table VIII show a total range of greater than 10^4 from the least reactive primary alkyl hydrogen atom abstraction to the most reactive addition reaction. The aromatic compounds show a wide range of reactivities because of the exceptionally low reactivity of benzene.

Comparison of Relative Rates of Reaction in Liquid and Gas Phase. Table IX compares the relative rate constants obtained in solution with the ratio of absolute rate constants[5] in the gas phase. The gas- and solution-phase rate constants correlate at the 1% level.[32] Thus, within the variation of the experimental results, the relative rate constants can be assumed equal for both the liquid and the gas phase. This point has been discussed in detail using the older data of Edwards and Mayo for the liquid-phase reactivities. (See, for example, p 164 in ref 30a.) These data made cyclo-

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(30) (a) W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966. (b) Szwarc used acetyl peroxide as a source of methyl radicals. We have used *tert*-butyl peracetate because it is a very much safer compound to handle; however, this required that we use a higher temperature than that used by Szwarc.

(31) Our values of $k_{\mathrm{addition}}/k_{\mathrm{abstraction}}$ are a factor of approximately three larger than those measured in the gas phase.[29] This discrepancy may be due to a systematic error in combining our $k_{\mathrm{iso}}/k_{\mathrm{SD}}$ value with Szwarc's $k_{\mathrm{add}}/k_{\mathrm{iso}}$ value. There is good agreement between Szwarc and Cvetanović on the *relative* rates of addition to various olefins.

(32) W. J. Dixon and F. J. Massey, "Introduction to Statistical Analysis," 2nd ed, McGraw-Hill, New York, N. Y., 1957.

Table IX. Relative Reactivities of Various Hydrogen Donors with Methyl Radicals at 110° in Gas and Liquid Phases[a]

Hydrogen donor, RH	$k_{RH} \times 10^{-3}$ (gas)	k_{RH}/k_{hexane} Gas	Soln	Ratio gas phase to soln	Calcd value $k_{RH} \times 10^{-3}$ (gas)[b]
Hexane	2.9	1.0	1.0	1.0	2.9
2,3-Dimethylbutane	7.3	2.5	3.0	0.85	8.8
Cyclopentane	4.7	1.6	1.0	1.5	3.0
Cyclohexane	3.6	1.3	1.0	1.2	3.0
Toluene	1.8	0.61	0.77	0.77	2.3
Ethylbenzene	6.7	2.3	2.3	1.0	6.7
Cumene	12.0	4.3	3.6	1.2	11
p-Xylene	3.9	1.4	1.8	0.79	5.2

[a] Data have been rounded to two significant figures; see text. [b] See text for method of calculation. Units are M^{-1} sec^{-1}.

hexane appear to be anomalous, but this now appears to be due to an error in the older data.

Equating the relative reactivities in the gas phase to those in the liquid phase gives

$$k_{RH}(g) = k_{SD}(g)[k_{RH}/k_{SD}]_{sol}$$

where $k_{SD}(g)$ is the calculated absolute rate constant in the gas phase, $k_{RH}(g)$ is the experimental absolute rate constant, and $[k_{RH}/k_{SD}]_{sol}$ is the ratio of relative rate constants in the liquid phase at 110°. Values of $k_{RH}(g)$ and $[k_{RH}/k_{SD}]_{sol}$ found in Table IX were used to calculate $k_{SD}(g)$. Excluding cyclopentane, the average value of $k_{SD}(g)$ is $(1.42 \pm 0.28) \times 10^5$ M^{-1} sec^{-1}. Absolute rate constants for the gas phase can then be calculated if the relative reactivity in the liquid phase is known. Recently, Greiner[33] proposed a general formula for predicting the reactivity of methyl radicals in the gas phase; unfortunately, it is restricted to alkanes.

Limitation of Relative Reactivities. The values of unity at the top of each column in Table VI are shown in parentheses since they are not necessarily equal to each other in absolute value. For example, the absolute value of the rate constant for reaction of secondary alkyl hydrogens with the methyl radical (column 2) cannot be compared with the value for the phenyl radical (column 4) since the methyl radical data are relative to k_{SD} and the phenyl[34] to k_{CCl_4}.

Furthermore, the relative values of k_H are comparable in a single vertical column only if the specific rate constant for the standard reaction is the same in all reaction mixtures. Burkhart[35] determined the absolute rate constant for the following reaction

$$C_3H_7\cdot + RSH \longrightarrow C_3H_8 + RS\cdot$$

He reported that when the cosolvent is changed from benzene to cyclohexane, the absolute rate constant changes from 3×10^4 to 2.9×10^6 M^{-1} sec^{-1}. We expect, therefore, that the magnitude of k_{SD} will vary somewhat when the cosolvent changes and that the k_{RH}/k_{SD} values are comparable in a single column only when similar cosolvents are used.

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(33) N. R. Greiner, *J. Chem. Phys.*, **53**, 1285 (1970).

(34) W. A. Pryor, J. T. Echols, and K. Smith, *J. Amer. Chem. Soc.*, **88**, 1189 (1966).

(35) R. D. Burkhart, *J. Phys. Chem.* **73**, 2703 (1969).