cooling the mixed ureas 12–14 of Table I crystallized out and were purified by one recrystallization from ligroin (bp 60–70°).

Registry No.—2, 19202-78-9; 2 oxime, 19202-79-0; 3, 19203-41-9; 3 oxime, 19203-42-0; 6, 19203-43-1.

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Relative Rate Constants for Hydrogen Abstraction by Methyl Radicals from Substituted Toluenes[1,2]

William A. Pryor, Umberto Tonellato,[3a]
Daniel L. Fuller,[3b] and Sandra Jumonville

Louisiana State University, Department of Chemistry,
Baton Rouge, Louisiana 70803

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Atom abstraction is the most common reaction which radicals undergo, and hydrogen is the most commonly transferred atom.[4a] For this reason, it is important to amass data which can lead to mechanistic insights into the factors influencing this process. Recently, extensive studies have been reported of hydrogen abstraction by the phenyl and *p*-nitrophenyl radicals in solution.[5] There are extensive data on the methyl radical in the gas phase;[6] however, until recently the only data on hydrogen abstraction by methyl radicals in solution were the very limited data of Edwards and Mayo.[7a] Recently, Mayo[7b] himself, as well as other authors, have emphasized the importance of repeating this work. Some data have recently been published by Szwarc[8] and by Berezin and Dobish.[9] In this communication we present data on the Hammett correlation for the reaction of methyl with substituted toluenes. We conclude that methyl is a slightly electrophilic radical; the Hammett equation for abstraction from toluenes by methyl radicals gives a value of ρ^+ of about -0.1. Surprisingly, this is very near the value which correlates data for abstraction by the phenyl radical.[5] We briefly discuss our attempts to obtain relative rate constants for hydrogen abstraction from aliphatic hydrogen donors. For these solvents, the relative values of k_H are solvent dependent.

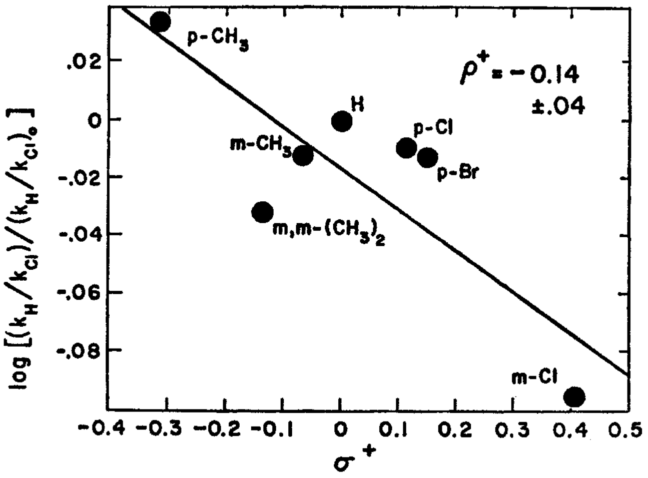

Figure 1.—The Hammett plot for the reaction of methyl radicals with substituted toluenes. The line shown is that given in eq 5 in the text.

We have used the experimental design originated by Edwards and Mayo in which 0.1 *M* solutions of acetyl peroxide are allowed to decompose in a mixed solvent consisting of carbon tetrachloride and a hydrogen donor, and the ratio of CH_4 and CH_3Cl in the products is related to k_H/k_{Cl} (eq 1 and 2). Edwards and Mayo

$$CH_3\cdot + RH \xrightarrow{k_H} CH_4 + R\cdot \tag{1}$$

$$CH_3\cdot + CCl_4 \xrightarrow{k_{Cl}} CH_3Cl + \cdot CCl_3 \tag{2}$$

used a complex gas separation procedure to obtain their analyses. We have used a technique in which 5 to 10 μl of the reaction solution is placed in a capillary tube, which is deaired, and sealed, and placed in a 100° bath, and allowed to react. The capillary is then crushed in the gas stream of an Aerograph Model 202-1 gas chromatograph using a Hewlett–Packard "Solid Sample Analyzer." A $\frac{1}{8}$ in. × 10 ft column of Porapac allows separation and analysis of the following components: CO_2, CH_4, CH_3Cl, C_2H_6, methyl acetate, carbon tetrachloride, and chloroform. The molar response of the gases was determined using both known amounts of the pure gases and standard mixtures made up on a vacuum line.[10]

In agreement with Edwards and Mayo,[7a] we find that some CH_4 is produced even when 0.1 *M* acetyl peroxide is allowed to decompose in pure CCl_4, and a correction must be applied in the mixed solvents for this methane.[5] We have calculated k_H/k_{Cl} values using eq 3 where

$$k_H/k_{Cl} = \frac{CH_4/CO_2 - M_0}{CH_3Cl/CO_2} R_0 \tag{3}$$

$R_0 = X_{CCl_4}/X_{RH}$ (X is the mol fraction[8c]) and $M_0 = (CH_4/CO_2)_0$ is the amount which must be subtracted to correct for the methane which does not arise from reaction 1. Using three values of R_0 and toluene as the hydrogen donor, the value of k_H/k_{Cl} is most nearly constant if M_0 is taken as 3.5% relative to CO_2 as 100.[11]

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[1] Reactions of Radicals. 22.

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[3] (a) Postdoctoral Fellow supported by a grant from the Air Force Office of Scientific Research, AFOSR(SRC)-OAR, 1964–1966. (b) National Science Foundation College Teacher Research Participant, 1966–1968.

[4] W. A. Pryor, "Free Radicals," McGraw-Hill Book Co., New York, N. Y., 1966: (a) pp 150–175; (b) pp 87–90; (c) p 172; (d) p 364.

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[6] For reviews, see (a) A. F. Trotman-Dickenson, "Free Radicals," Methuen and Co. Ltd., London, 1959; (b) "Gas Kinetics," Butterworth and Co. (Publishers) London, 1955.

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[10] Our analytical results have been confirmed for a number of runs by mass spectrographic analysis.

[11] Edwards and Mayo,[7a] found M_0 to be 0.035 mmol/mol of peroxide decomposed, or approximately 2.7% of the CO_2 yields, by a different method.

TABLE I

REACTION OF METHYL RADICALS WITH ARALKYL HYDROGEN DONORS AND CARBON TETRACHLORIDE MIXTURES AT 100°

Hydrogen donor, RH	X_{CCl_4}/X_{RH}[a]	Moles formed/100 mol of CO_2				n[b]	k_H/k_{Cl}
		CH_4	C_2H_6	CH_3Cl	CH_3OAc		
Toluene	0.44	31.3	4.6	41.6	13.6	8	0.29
Toluene	0.47	28.5	4.0	41.6	13.6	4	0.28
Toluene	0.81	22.3	4.2	51.2	14.3	12	0.30
Toluene	1.61	14.9	4.4	62.2	14.5	6	0.30
Ethylbenzene	0.44	48.9	4.4	26.6	14.8	5	0.74
Ethylbenzene	0.82	38.3	4.2	36.5	14.2	5	0.76
Ethylbenzene	1.62	28.4	4.3	47.9		4	0.82
Cumene	0.47	56.4	4.4	19.2		3	1.29
p-Phenoxytoluene	0.41	21.7	5.2	32.0	42	4	0.23
p-Phenoxytoluene	0.60	17.8	5.3	40.0	44	3	0.21
p-Xylene[c]	0.44	42.0	4.0	26.7	15.9	5	0.63
p-Xylene[c]	0.65	37.0	4.2	34.3	15.6	3	0.63
m-Xylene[c]	0.43	41.2	4.0	27.8	17.6	3	0.58
m-Xylene[c]	0.65	35.1	4.2	36.4	18.7	3	0.56
p-Chlorotoluene	0.41	27.4	4.2	35.3	21	4	0.27
p-Chlorotoluene	0.54	26.0	4.7	40.2		3	0.30
p-Bromotoluene	0.41	25.9	5.2	33.0	21	4	0.27
p-Bromotoluene	0.60	21.9	5.6	36.7	21	3	0.29
m-Chlorotoluene	0.42	24.7	4.4	36.8		3	0.24
m-Chlorotoluene	0.58	20.8	4.1	42.3		2	0.23

[a] Ratio of the mole fraction of CCl_4 to RH in the reaction solution. [b] Number of duplicate runs. [c] The value plotted in Figure 1 has been statistically corrected by dividing by 2.

With ethylbenzene as the hydrogen donor, three values of R_0 gave $M_0 = 4.3\%$ of CO_2. In the calculations in Table I we have used these values of M_0: 0.035 for toluene, 0.043 for ethylbenzene, and an average of 0.039 for the remainder of the solvents. The precise value of M_0 does not affect the value of k_H/k_{Cl} by more than 5%.

We have studied a wide range of hydrogen donors. However, the k_H/k_{Cl} values for substrates which do not possess an aromatic ring are not independent of the solvent ratio. We, therefore, will discuss our data on aromatic solvents first and will return to a consideration of the nonaromatic donors. Table I gives the data and Figure 1 shows the Hammett plot for the reaction of methyl radicals with substituted toluenes. The least-square equations using σ and σ^+ are the following.[12]

$$\log \frac{(k_H/k_{Cl})}{(k_H/k_{Cl})_0} = (-0.121 \pm 0.062)\sigma - (0.010 \pm 0.001) \qquad (4)$$

$$\log \frac{(k_H/k_{Cl})}{(k_H/k_{Cl})_0} = (-0.139 \pm 0.045)\sigma^+ - (0.015 \pm 0.009) \qquad (5)$$

Figure 1 shows the correlation with σ^+ since this parameter is most often used to correlate radical reactions.[4c] Clearly, methyl radicals have very little polar character, and the value of ρ is too small to either distinguish σ from σ^+ meaningfully or to allow determination of ρ with great precision. Nevertheless, the Hammett correlation is a convenient way to capsulize the polar character of radical species, and in this sense the value $\rho \cong -0.1$ for methyl is quite descriptive. The phenyl radical gives about the same value of ρ;[5] *p*-nitrophenyl, in contrast, is appreciably electrophilic.[5b] Methyl and phenyl radicals also appear quite similar in their reactions with the series toluene/ethylbenzene/cumene. Our data give the relative k_H value *per reactive benzylic hydrogen* for the methyl radical to be 1:3.9:12.9. This agrees closely with Szwarc[8a,b] who reported 1:4.0:12. This pattern[5a] for the phenyl radical is 1:4.6:9.7. The more selective *p*-nitrophenyl radical[5b] gives the pattern 1:6.3:26. The striking similarities in the phenyl and methyl radicals in these reactions are surprising in view of the differing electronegativities of the two groups and of the differing bond dissociation energies of CH_3–H and of C_6H_5–H.[13]

We now wish to discuss our data on aliphatic solvents. We observed that the k_H/k_{Cl} values for alkanes and cycloalkanes are not independent of the solvent ratio R_0. For these solvents, we also observed that amounts of chloroform were produced which were up to ten times greater than the amounts of the $\cdot CCl_3$ radical produced in eq 2. It is clear that some chain process produces chloroform in these solvents, and we suggest eq 6 and 7. This sequence prohibits the use of eq

$$R\cdot + CCl_4 \rightarrow RCl + \cdot CCl_3 \qquad (6)$$

$$\cdot CCl_3 + RH \rightarrow HCCl_3 + R\cdot \qquad (7)$$

3 to obtain relative k_H values for two reasons. First, so much CCl_4 is used that its concentration does not remain constant during an experiment. Second, the chloroform which is produced is a surprisingly good

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[12] (a) The point for *p*-phenoxytoluene has been omitted from the correlation. The σ^+ value for this substituent is uncertain; it has been reported to be −0.57 by G. A. Russell and R. C. Williamson [*J. Amer. Chem. Soc.*, **86**, 2357 (1964)] and −0.899 by C. G. Swain and E. C. Lupton, Jr. [*ibid.*, **90**, 4328 (1968)]. Regardless of which of these values is chosen, however, the correlation requires that the *p*-phenoxy substituent increase the rate constant, whereas actually *p*-phenoxytoluene reacts with methyl radicals more slowly than does toluene. This pattern has been observed before. For example, *p*-phenoxytoluene reacts more slowly than does toluene with phenyl radicals.[5a] It reacts at about the same rate as does toluene and much more slowly than predicted by the Hammett plot, with the *p*-nitrophenyl radical.[5b] It reacts somewhat faster than toluene, but again much more slowly than predicted from the Hammett plot, with the peroxy radical (Russell and Williamson, reference cited above). (b) The application of eq 8 requires that ethane and methyl acetate are produced exclusively in cage reactions which occur independently of the partition of methyl between RH and CCl_4 in free solution.[4b] The data in Table I support this assumption for all the solvents except *p*-phenoxytoluene which has a higher viscosity and appears to be anomalous. (c) The mesitylene point in Figure 1 is from ref 8a. Inclusion of this point hardly affects the value of ρ or the goodness of it. For example, without this point and using σ^+, ρ is (-0.161 ± 0.037) and the intercept is (-0.008 ± 0.008).

[13] The value of $D(CH_3\text{–}H)$ is 104[14]. The value of $D(C_6H_5\text{–}H)$ is 112: A. S. Rogers, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, **89**, 4578 (1967).

hydrogen donor; much better, in fact, than are most of the RH compounds. By measuring the yields of methane and chloromethane from reaction of acetyl peroxide in mixtures of chloroform and carbon tetrachloride, we obtained these ratios of rate constants: $k_H/k_{Cl} = 160$; $k_H/k_{Cl}' = 53$; $k_{Cl}'/k_{Cl} = 3.2$, where k_H is the rate constant for abstraction of hydrogen from $CHCl_3$, k_{Cl}' is that for abstraction of chlorine from $CHCl_3$, and k_{Cl} is that for abstraction of chlorine from CCl_4. Thus, even fairly short chain lengths for reactions 6 and 7 could produce sufficient $CHCl_3$ to seriously affect the apparent k_H/k_{Cl} value obtained for RH. These conclusions are in accord with the findings of DeTar[15] who studied the hexyl radical using reaction with CCl_4 as the standard. He also found that for aliphatic solvents, $\cdot CCl_3$ reacts with RH to produce $CHCl_3$ and RCl in a reaction with an appreciable chain length.

The difficulty in using CCl_4 as the standard substrate for aliphatic but not for aromatic solvents can be rationalized by a consideration of the heats of reactions 6 and 7. For RH equal to ethane, the heats are -8 and $+2$ kcal/mol, for reactions 6 and 7, respectively; for toluene as RH, the heats are $+5$ and -11.[14] Thus, the chain sequence 6 and 7 is blocked for aromatic donors by the high enthalpy, and consequently high activation energy, of reaction 6. It would appear that this difficulty could be circumvented by using a standard substrate which has a higher bond strength than does CCl_4; unfortunately, this does not appear to be the case. Berezin and Dobish[9b] used the reaction of methyl radicals with tritiated heptane as their standard reaction. However, Table I of their publication[9b] shows that their values of the relative rate constant for hydrogen abstraction also are quite solvent dependent. At present, therefore, there is no satisfactory method for putting the relative rate constants for abstraction of hydrogen from aliphatic and aromatic solvents on the same scale.

This has one important consequence. The relative rate constants measured by Edwards and Mayo are widely quoted and are compared with data for the reaction of methyl radicals in the gas phase. It is often pointed out that the only solvent which appears to give a relative rate constant in solution which does not parallel the gas phase data is cyclohexane.[4d,7b,15,16] This solvent is, in fact, the only solvent studied by Edwards and Mayo which is saturated. It would appear, therefore, that the Edwards and Mayo value of k_H/k_{Cl} for cyclohexane is not reliable; in fact, we find that this value is solvent dependent.

Finally, it is interesting to consider a consequence of the simple mechanism indicated by eq 1 and 2. If eq 1 is the only important methane-producing reaction, and if all the *free* methyl radicals[12b] react either with the hydrogen donor RH or with CCl_4, then one should be able to calculate k_H/k_{Cl} as in eq 8 where M_0 has the same

$$k_H/k_{Cl} = \frac{CH_4/CO_2 - M_0}{[CH_4/CO_2]_{ps} - CH_4/CO_2} R_0 \qquad (8)$$

meaning as before and $[CH_4/CO_2]_{ps}$ is the relative yield of methane obtained in the pure hydrogen donor as solvent.[17] We find that eq 3 and 8 give essentially the same values of k_H/k_{Cl} for aromatic substrates but give very different values for aliphatic donors. This again indicates the solvent dependence of the relative k_H values in aliphatic solvents. Clearly, it is better to calculate k_H/k_{Cl} values using eq 3, but the agreement between eq 3 and 8 gives confidence that this system does yield a simple partition of free methyl radicals between reaction with RH or CCl_4 in aromatic solvents.

Registry No.—Methyl radical, 2229-07-4; toluene, 108-88-3; ethylbenzene, 100-41-4; cumene, 98-82-8; *p*-phenoxytoluene, 1,706-12-3; *p*-xylene, 106-42-3; *m*-xylene, 108-38-3; *p*-chlorotoluene, 106-43-4; *p*-bromotoluene, 106387; *m*-chlorotoluene, 108418.

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(16) Reference 6a, p 70.

(17) We have measured the value of CH_4/CO_2 in these pure solvents: toluene, 0.730; *p*-xylene, 0.682; *p*-bromotoluene, 0.495 (also see ref 8e). We have used the toluene value for toluene, ethylbenzene, and cumene, the xylene value for both xylenes, and the bromobenzene value for all other solvents in eq 8.

Additions of Sulfenyl Chlorides to Acetylenes. XII.[1a] Addition to *t*-Butylacetylene[1b]

V. Caló, G. Scorrano, and G. Modena[1c]

Istituto di Chimica Organica, Università di Bari, Padova, Italy

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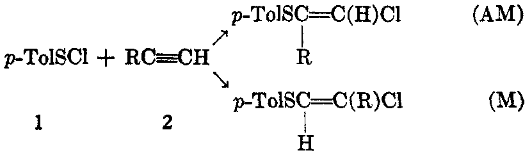
Both Markovnikov (M) and anti-Markovnikov (AM) orientations have been observed in the addition of *p*-toluensulfenyl chloride to acetylenes[2] depending on the nature of the acetylene and on the solvent (with



$$\underset{\mathbf{1}}{p\text{-TolSCl}} + \underset{\mathbf{2}}{RC{\equiv}CH} \begin{cases} \nearrow \ p\text{-TolS}\underset{\substack{|\\ R}}{C}{=}C(H)Cl & (AM) \\ \searrow \ p\text{-TolS}\underset{\substack{|\\ H}}{C}{=}C(R)Cl & (M) \end{cases}$$

R = alkyl, 100% AM in all solvents;[3,4] with R = phenyl, 100% AM in ethyl acetate, 29% AM and 71% M in acetic acid). The effects are such that the phenyl substitution at the acetylenic carbons and good hydrogen bonding solvents[5] favor a shift from AM to M addition.

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[1] (a) Part XI: L. Di Nunno and G. Scorrano, *Ric. Sci.*, **38**, 343 (1968). (b) This work has been supported by a grant from the Consiglio Nazionale delle Ricerche, Roma. (c) To whom all correspondence should be addressed at the Istituto di Chimica Organica, Via Marzolo, 1, Padova, Italy.

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[3] Small amounts of M-type adducts have been observed in the addition to alkylacetylenes of *o*-nitrobenzensulfenyl chloride[2] and dimethylaminosulfenyl chloride.[4]

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