constants[7,8] yielded the correlations: log (k_p^{br}/M^{-1} sec^{-1}) = $-0.78\sigma - 1.4$ ($r = -0.93$) and log (k_p^{br}/M^{-1} sec^{-1}) = $-0.56\sigma^+ - 1.5$ ($r = -0.97$), respectively.[11] The influence of the substituents may be due to differences in the resonance stabilization energies of the ring-substituted benzyl radicals or to polar contributions to the transition states or possibly to contributions from both of these effects.

If it is accepted that differences in k_p^{br} are due to differences in D[R–H], values of 82 and 86 kcal/mol for D[p-$CH_3OC_6H_4CH_2$–H] and D[p-$NO_2C_6H_4CH_2$–H], respectively, can be calculated from eq 2. This implies that p-$CH_3OC_6H_4CH_2$ is stabilized by ~3 kcal/mol and p-$NO_2C_6H_4CH_2$ is *destabilized* by ~1 kcal/mol relative to $C_6H_5CH_2\cdot$. It also implies that m-$CNC_6H_4CH_2\cdot$ and m-$NO_2C_6H_4CH_2\cdot$ are both destabilized by ~1.5 kcal/mol. p-Methylacetophenone is 1/7th as reactive as p-methyltoluene which cannot be due to a lower bond strength since it has been shown[14] that the C–H bond strength in acetone is the same as in ethane.

It has been suggested[15] that para-substituted compounds should not be considered in the use of log (relatively reactivity) *vs.* σ or σ^+ plots to investigate polar effects, since radical stabilization must play an important role in determining reactivity. There can, however, be no such radical stabilization contribution from meta-substituted radicals. A plot of log (k_p^{br}) for the five meta-substituted toluenes against σ constants gave the correlation, log (k_p^{br}/M^{-1} sec^{-1}) = $-0.76\sigma_m - 1.49$ ($r = 0.99$). It should be possible to estimate from this correlation and the appropriate σ_p^+ constant values of the rate constant for abstraction of a H-atom from ring-substituted toluenes by t-BuOO·, $(k_p^{br})_{est}$, that are free from a contribution due to resonance stabilization. For example, $(k_p^{br})_{est}$ for p-methoxytoluene = 0.13 M^{-1} sec^{-1} and for p-nitrotoluene = 0.008 M^{-1} sec^{-1}; comparison of these values with experimentally determined values of k_p^{br} implies that the p-methoxybenzyl and benzyl radicals have virtually the same resonance stabilization energies, while the p-cyano- and p-nitrobenzyl radicals are more stable than benzyl by *ca.* 500 cal/mol.

Hydrogen abstraction from toluene by t-BuOO· will be exothermic by 3 kcal/mol and by Br by 2.5 kcal/mol.[16] According to Zavitsas and Pinto's argument[5] the ρ values for abstraction from ring-substituted toluenes by these two radicals should be very similar. Since this is not the case, *i.e.*, $\rho^+(t\text{-BuOO}\cdot) = -0.56$ and $\rho(\text{Br}\cdot) = -1.5$ to -1.7,[20] it must be concluded that the correlation of ρ with ΔH for the five radicals is fortuitous. A difference in ρ between two radicals with the same ΔH cannot be attributed to resonance stabilization. It seems most reasonable to invoke polar effects to explain the larger ρ value for Br· which is more electrophilic than t-BuOO .

The results of this work would, therefore, appear to support the suggestion made nearly 20 years ago by Russell and Brown[21] that the rates of hydrogen atom transfer reactions may be influenced by polar effects.[22] Further confirmation of this concept has been obtained very recently by Pryor, *et al.*[23] These workers have found that the reaction of *tert*-butyl radicals with ring-substituted toluenes has a *positive* ρ value of about 1.3. On the basis of Zavitsas and Pinto's arguments, positive ρ values for abstractions from toluenes should be impossible.

Acknowledgment. The authors wish to thank Dr. Zavitsas for the opportunity to see his manuscript prior to publication and Dr. K. U. Ingold for many fruitful discussions on this topic.

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(7) As quoted in H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **80**, 4979 (1958).

(8) Hammett and Brown substituent constants were chosen because they have been favored by researchers in the field of H-atom abstraction reactions. It would, however, be more appropriate to use Yukawa and Tsuno's[9] modification of the Hammett equation. This gave the correlation: log (k_p^{br}/M^{-1} sec^{-1}) = $-0.61(\sigma^0 + 0.77\Delta\bar{\sigma}_R^+) - 1.47$ ($r = -0.98$), where $\Delta\bar{\sigma}_R^+$ ($= \sigma^+ - \sigma^0$) is the substituent resonance parameter and the resonance reaction constant (r^+) = 0.77. The values of σ^0 used for this correlation were taken from ref 9b (the para substituents) and ref 10 (the meta substituents).

(9) (a) Y. Yukawa and Y. Tsuno, *Bull. Chem. Soc. Jap.*, **32**, 965, 971 (1959); (b) Y. Yukawa, Y. Tsuno, and M. Sawada, *ibid.*, **39**, 2274 (1966).

(10) H. van Bekkum, P. E. Verkade, and B. M. Wepster, *Recl. Trav. Chim. Pays. Bas.*, **78**, 815 (1959).

(11) Attempts have been made to derive an extended Hammett equation[12] of the form log $(k/k^0) = \rho\sigma - \gamma E_R$ to separate polar ($\rho\sigma$) and resonance (γE_R) contributions to free-radical reactions. The use of special E_R values, however, does not seem justified.[13]

(12) R. Itô, T. Migita, N. Morikawa, and O. Simamura, *Tetrahedron*, **21**, 955 (1965); (b) T. Yamamoto and Y. Otsu, *Chem. Ind. (London)*, 787 (1967); (c) H. Sakurai, S. Hayashi, and A. Hosomi, *Bull. Chem. Soc. Jap.*, **44**, 1945 (1971).

(13) A. P. G. Kieboom, *Tetrahedron*, **28**, 1325 (1972).

(14) (a) R. K. Solly, D. M. Golden, and S. W. Benson, *Int. J. Chem. Kinet.*, **2**, 11 (1970); (b) K. P. King, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, **92**, 5541 (1970).

(15) See, *e.g.*, M. DaRooge and L. R. Mahoney, *J. Org. Chem.*, **32**, 1 (1967).

(16) Taking $D[t\text{-BuOO–H}] = 88$,[17] $D[C_6H_5CH_2\text{–H}] = 85$,[18] and $D[\text{Br–H}] = 87.5$ kcal/mol.[19]

(17) L. R. Mahoney and M. A. DaRooge, *J. Amer. Chem. Soc.*, **92**, 4063 (1970).

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

(19) A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," 3rd ed, Chapman and Hall, London, 1968.

(20) (a) R. E. Pearson and J. C. Martin, *J. Amer. Chem. Soc.*, **85**, 3142 (1963); (b) C. Walling, A. L. Rieger, and D. D. Tanner, *ibid.*, **85**, 3129 (1963); (c) E. C. Kooyman, R. Van Helden, and A. F. Bickel, *Proc., Kon. Ned. Akad. Wetensch., Ser. B*, **56**, 75 (1953).

(21) G. A. Russell and H. C. Brown, *J. Amer. Chem. Soc.*, 77, 4578 (1955).

(22) For a recent comprehensive review on the influence of reactivity, selectivity, and polar effects on hydrogen atom transfer reactions see G. A. Russell, "Free Radicals," Vol. 1, J. K. Kochi, Ed., Wiley, New York, N. Y., 1963, Chapter 7.

(23) W. A. Pryor, W. H. Davis, Jr., and J. P. Stanley; private communication of work presented at the 165th National Meeting of the American Chemical Society, Dallas, Tex., April 1973.

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On Hydronium Ion Activity in Strongly Acidic Media. A Remarkable Agreement between Independent Estimates

Sir:

We have recently reported[1] estimates of the hydronium ion activity in aqueous sulfuric acids up to 70% acid. These were based on five independent acidity scales, combined with independently measured activity coefficient data on appropriate model indicator species, using the relation

$$\log a^*_{H^+} = -H_X - \log f_X + \log f^*_{XH^+}$$

Since the model cation activity coefficients are neces-

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(1) K. Yates, H. Wai, G. Welch, and R. A. McClelland, *J. Amer. Chem. Soc.*, **95**, 418 (1973).

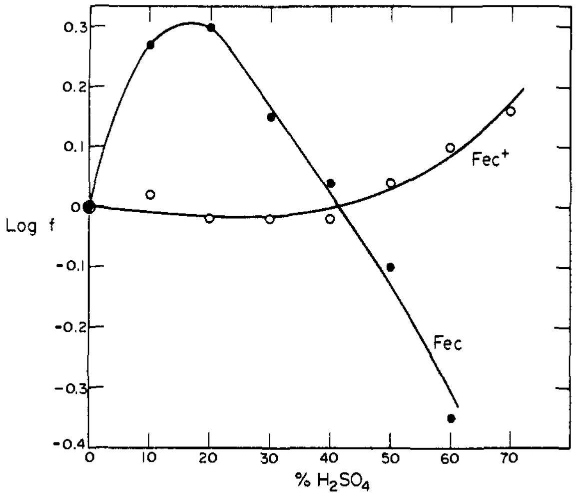

Figure 1. Logarithmic activity coefficient variation with sulfuric acid concentration for ferrocene (Fec) and ferricinium ion (Fec$^+$).

sarily referred to some standard ion, using the Boyd approximation,[2] the resulting hydronium ion activities are thus referred to the same standard ion, in this case tetraethylammonium (TEA$^+$).[3] Hence, log $a^*_{\mathrm{H}^+}$ = log $a_{\mathrm{H}^+}/f_{\mathrm{TEA}^+}$. The internal agreement between the five independent estimates of log $a^*_{\mathrm{H}^+}$ was remarkably good in view of the approximations involved, and mean values of log $a^*_{\mathrm{H}^+}$ at 10% intervals in H_2SO_4 are listed in Table I.

Table I. Activities and Activity Coefficients in Sulfuric Acid at 25°

% acid	Log $a^*_{\mathrm{H}^+}$ [a,g]	$-H_{\mathrm{GF}}$ [b]	+Log f_{Fec^+} [c]	−Log f_{Fec}	Log $a^*_{\mathrm{H}^+}$ [d,g]	Δ
10	0.52	0.44	0.02	−0.27	0.19	0.33
20	1.55	1.61	−0.02	−0.30	1.29	0.26
30	2.80	2.68	−0.02	−0.15	2.51	0.29
40	4.23	3.88	−0.02	−0.04	3.82	0.41
50	5.85	5.33	+0.04	+0.10	5.47	0.38
60	7.69	7.00	+0.10	+0.35	7.45	0.24
70	9.66	9.25[e]	+0.16	+0.45[f]	9.86	−0.20

[a] Mean values from ref 1, relative to f_{TEA^+}. [b] Interpolated from ref 4. [c] From ref 5. [d] Calculated from log $a^*_{\mathrm{H}^+} = -H_{\mathrm{GF}}$ + log $f^*_{\mathrm{Fec}^+}$ − log f_{Fec}. [e] Value subject to possible error due to partial protonation of ferrocene. [f] Obtained by a short extrapolation. [g] The values of log $a^*_{\mathrm{H}^+}$ in columns 2 and 6 correlate against each other with $r = 0.999$ and $\sigma_y = 0.17$.

Another method of estimating hydronium ion activity in aqueous sulfuric acid has recently been reported by Janata and Jansen.[4] These authors employed a combined polarographic–glass electrode approach, involving no liquid junction, and used the ferrocene–ferricinium ion (Fec–Fec$^+$) couple as reference electrode. It is therefore of considerable interest to determine to what extent these two independent methods of estimating hydronium ion activity in concentrated acid give concordant results. Values of the glass–ferrocene function $-H_{\mathrm{GF}}$, interpolated from Janata and Jansen's data, are also listed in Table I.

Before the two functions log $a^*_{\mathrm{H}^+}$ and $-H_{\mathrm{GF}}$ can be compared, it is important to note that the latter function is based[4] on the difference between the ferrocene half-wave potential ($E_{1/2}$) and the glass electrode potential (E_g) and is defined by

$$-H_{\mathrm{GF}} = \frac{F}{2.303RT}[(E^\circ_{1/2} - E_{1/2}) - (E^\circ_g - E_g)] =$$

$$\log a_{\mathrm{H}^+} + {}^1/_2 \log \frac{D_{\mathrm{Fec}^+}}{D_{\mathrm{Fec}}} + \log f_{\mathrm{Fec}}/f_{\mathrm{Fec}^+}$$

where the E° are standard potentials, D are diffusion coefficients, and the f's refer to activity coefficients. For $-H_{\mathrm{GF}}$ to be a valid measure of log a_{H^+}, it is essential that both the ratio of diffusion coefficients and of activity coefficients be constant, independent of the medium. As pointed out by Janata and Jansen,[4] it seems unlikely that variations in log $D_{\mathrm{Fec}^+}/D_{\mathrm{Fec}}$ will cause deviations outside experimental error. However, the medium variation of log $f_{\mathrm{Fec}}/f_{\mathrm{Fec}^+}$ can be tested. Values of log $f^*_{\mathrm{Fec}^+}$ (relative to TEA$^+$) are available,[5] and we have now measured values of log f_{Fec} in sulfuric acid using a distribution method.[2] These data are plotted in Figure 1, where it can be seen from the curves that the ratio log $f_{\mathrm{Fec}}/f^*_{\mathrm{Fec}}$ is clearly medium dependent,[6] since ferrocene salts out initially, where the ferricinium ion data are essentially constant, and then salts in strongly in more concentrated acids, where ferricinium ion is just beginning to salt out. Thus the medium dependence of $f_{\mathrm{Fec}}/f_{\mathrm{Fec}^+}$ will be incorporated into $-H_{\mathrm{GF}}$, which is then effectively defined by

$$-H_{\mathrm{GF}} = \log a_{\mathrm{H}^+} f_{\mathrm{Fec}}/f_{\mathrm{Fec}^+}$$

A direct comparison with log $a^*_{\mathrm{H}^+}$ can now be made by subtracting out from $-H_{\mathrm{GF}}$ the contributions due to f^*_{Fec} and f_{Fec^+}. This will bring both scales to the same reference basis (f_{TEA^+}) and the following equation should hold if the two methods give concordant results.

$$\log a^*_{\mathrm{H}^+} + (H_{\mathrm{GF}} - \log f^*_{\mathrm{Fec}^+} + \log f_{\mathrm{Fec}}) = 0$$

Values of the left-hand side of this equation are given in Table I from 10 to 70% H_2SO_4. It can be seen that this quantity (Δ), although nonzero, does not differ vary significantly from zero, varying from −0.2 to +0.4 with a standard deviation of +0.3.[7] The agreement between the two approaches must be considered highly satisfactory, especially in view of the fact that both

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(2) R. H. Boyd, *J. Amer. Chem. Soc.*, **85**, 1555 (1963).

(3) R. H. Boyd in "Solute Solvent Interactions," J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N. Y., 1969, p 97.

(4) J. Janata and G. Jansen, *J. Chem. Soc., Faraday Trans. 1*, 1656 (1972).

(5) C. G. Swain and K. G. Harbison, unpublished results; K. G. Harbison, Ph.D. Thesis, Massachusetts Institute of Technology, 1966.

(6) Relative to TEA$^+$ at least, since single ion activities and hence ratios such as $f_{\mathrm{Fec}}/f_{\mathrm{Fec}^+}$ can never be measured absolutely.

(7) These differences (from zero), which remain after correcting both scales to the same reference (TEA$^+$), are almost certainly attributable to the method of estimating log $a^*_{\mathrm{H}^+}$ and not to the method of measuring H_{GF}.[8] However, although the latter method is more direct, and presumably less subject to error, the H_{GF} function, and hence the a_{H^+} values based on it, are referred to a less suitable standard ion, Fec$^+$. It appears the best approach would be to measure a_{H^+} directly using the polarographic–glass electrode technique, and then try to correct these values to a more suitable standard reference ion, such as TEA$^+$.

(8) It has been suggested by a referee that neglect of the diffusion coefficient term, 0.5 log $D_{\mathrm{Fec}^+}/D_{\mathrm{Fec}}$, might be responsible for the mainly positive values of Δ in Table I, even if this ratio were medium independent as assumed by Janata and Jansen.[4] For example, if the neutral ferrocene molecule had a larger diffusion coefficient than the ion in all solutions, as seems reasonable, this would contribute a constant positive term to Δ. However, the neutral molecule would need to have a diffusion coefficient about five times as large as that of the ion to account for the observed differences, which seems very unlikely.

$-H_{GF}$ and log $a^*_{H^+}$ vary over almost ten logarithmic units in the range of acid investigated.

It thus seems very hopeful that useful approximate values of hydronium ion activities in concentrated acid solutions can either be directly measured[4] or estimated.[1] The potential utility of such data in studying acid-catalyzed reactions is great, and is discussed in detail elsewhere.[9]

Acknowledgments. We are grateful to the National Research Council of Canada for financial support, and to Dr. J. Janata for helpful discussions.

(9) K. Yates and R. A. McClelland, *Progr. Phys. Org. Chem.*, in press.

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Anomalous Transition Metal Complex Promoted Rearrangement of Tricyclo[4.1.0.0^{2,7}]heptanes in Methanol[1]

Sir:

Our initial postulation[2] of the formation of a transition metal complexed carbene–transition metal bonded carbonium ion hybrid intermediate in the transition metal complex promoted rearrangement of derivatives of bicyclo[1.1.0]butanes[3] has now received substantial support.[4–8] Recently, Dauben and Kielbania confirmed our concept of an intermediate metal complexed carbene.[7] However, they questioned the validity of our suggestion[9] that a metal bonded cyclopropyl carbinyl cation might be a precursor of the observable metal complexed carbene. We now wish to report that transition metal complex promoted rearrangements of derivatives of bicyclo[1.1.0]butane in methanol are far more complex than either we or Dauben and Kielbania have indicated.

Whereas we had reported[9] that tricyclo[4.1.0.0^{2,7}]heptane[10] (**1**) gave a 75% yield of a mixture of **2** and **3** in methanol on addition of rhodium dicarbonyl chloride dimer, Dauben and Kielbania[7] showed that **1** gave 90% of **4**[11] and less than 10% of the mixture of **2** and **3** in methanol containing rhodium dicarbonyl chloride dimer and sodium bicarbonate. It was implied[7] that the apparent discrepancy between their finding and our results might be due to the use of aged rhodium dicarbonyl chloride dimer or to impure solvents. We have now found that the cause of this apparant discrepancy in results is associated with a much more fundamental aspect of the transition metal complex promoted rearrangement of bicyclo[1.1.0]butanes.[12] Our experiments indicated that the *product composition was determined by the rate of addition of the bicyclo[1.1.0]butane derivative to the methanol solution of rhodium dicarbonyl chloride dimer and sodium bicarbonate* and not by the other factors suggested.[7] When **1** was added to a methanolic solution of rhodium dicarbonyl chloride dimer (both in the presence and absence of sodium bicarbonate) a rapid and dramatic drop occurred in the "pH" of the methanolic solution.[13] The extent of this pH drop was extremely short-lived in the presence of sodium bicarbonate; the amount of time required to return to the normal pH was a function of the amount of **1** added at any one instant. Figure 1 shows the plots of the pH of the methanolic solution under various conditions. As can be seen from this plot the addition of rhodium dicarbonyl chloride dimer (15 mg) to methanol (3 ml), both with and without added sodium bicarbonate (10 mg), provides a drop of 4–5 pH units. In the absence of sodium bicarbonate, this lowered pH remains reasonably constant.

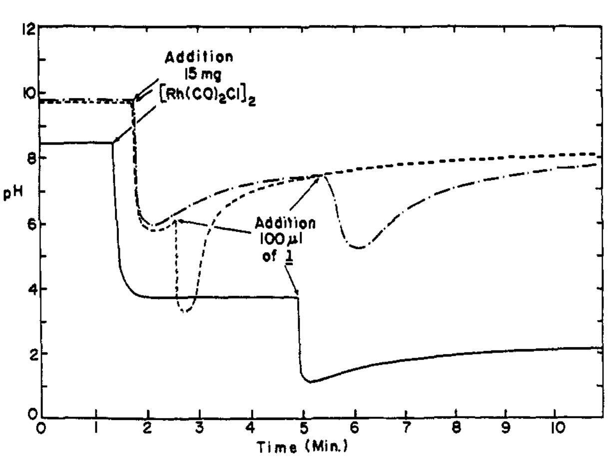
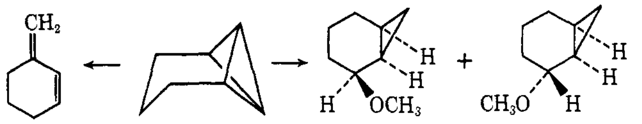


Figure 1. Plot of pH of a 3-ml sample of anhydrous methanol *vs.* time as a function of added sodium bicarbonate, added rhodium dicarbonyl chloride dimer, and added tricyclo[4.1.0.0^{2,7}]heptane. Solid line shows pH of methanol with no added sodium bicarbonate; dashed lines show plots of pH of methanol containing 10 mg of sodium bicarbonate per 3 ml of anhydrous methanol.



4 **1** **2** **3**

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(1) Paper XXXIX of a series on The Chemistry of Bent Bonds. For the preceding paper see P. G. Gassman and R. R. Reitz, *J. Organometal. Chem.*, in press.

(2) P. G. Gassman and F. J. Williams, *J. Amer. Chem. Soc.*, **92**, 7631 (1970); P. G. Gassman, T. Atkins, and F. J. Williams, *ibid.*, **93**, 1812 (1971).

(3) For a more recent discussion see P. G. Gassman and F. J. Williams, *ibid.*, **94**, 7737 (1972), and following papers.

(4) R. Noyori, T. Suzuki, Y. Kumagai, and H. Takaya, *ibid.*, **93**, 5894 (1971).

(5) P. G. Gassman and T. Nakai, *ibid.*, **93**, 5897 (1971).

(6) Of particular significance are recent low-temperature nmr studies of intermediate species. Both Dauben's[7] and Masamune's[8] groups have interpreted their nmr spectral data in terms of a metal complexed carbene intermediate or its resonance form, the transition metal bonded carbonium ion.

(7) W. G. Dauben and A. J. Kielbania, Jr., *J. Amer. Chem. Soc.*, **94**, 3669 (1972).

(8) S. Masamune, M. Sakai, and N. Darby, *J. Chem. Soc., Chem. Commun.*, 471 (1972).

(9) P. G. Gassman and T. J. Atkins, *J. Amer. Chem. Soc.*, **93**, 4597 (1971).

(10) W. R. Moore, H. R. Ward, and R. F. Merritt, *J. Amer. Chem. Soc.*, **83**, 2019 (1961).

(11) We had previously shown that **1** gave only **4** in nonprotic solvents.

(12) The results reported herein were reproducible with rhodium dicarbonyl chloride dimer which was (a) less than 2 hr old, (b) approximately 6 months old, and (c) a commercial sample (Strem Chemical) of unknown age and purity. Thus, the age of the complex is irrelevant. In all of our work solvent purity has been monitored with unusual care.

(13) The pH of the methanolic solution was monitored using a Metrohm-Herisau E-436 recording potentiometer with a Metrohm combination glass electrode EA-147. Ample precedent exists for the measurement of pH of methanolic solutions in this manner.[14]

(14) For leading references and discussions of the measurement of pH in methanol see: R. G. Bates, "Determination of pH-Theory and Practices," Wiley, New York, N. Y., 1964, Chapter 8. See also C. D. Ritchie and P. D. Heffley, *J. Amer. Chem. Soc.*, **87**, 5402 (1965).