actions as readily as does $IrCl(CO)P_2$.[8] Thus, it reacts relatively slowly with MeI, CF_3I, C_6F_5COCl, $MeSO_2Cl$, $PhCH_2Br$, PhCOCl, and MeSCN to form products which have not yet been fully characterized, but it reacts readily with CH_3COCl and CF_3COCl to form beautiful orange-yellow crystals of the stable 1:1 adducts. Though not conclusive evidence, infrared spectra suggest that the acetyl chloride compound is six coordinate and contains a chelating phenyl acetyl diazene.

$NO^+PF_6^-$ reacts with a methylene chloride solution of I to give an almost quantitative yield of $IrCl(NO)(PPh_3)_2^+$ and the diazonium salt. Thus, NO^+ binds more tightly than PhN_2^+ to Ir(I) by virtue of its better σ-electron donor characteristics. NOCl and Cl_2 react with I to give $IrCl_4P_2$ in good yields. I also reacts rapidly with NO_2^-, BH_4^-, NH_2^-, OH^-, Br_2, I_2, N_2H_4, $P(OPh)_3$, PF_3, MeCN, Et_2S, PhSH, PhC_2H, LiMe, and LiPh; it reacts more slowly with carboxylic acids, water, amines, Me_3SnCl, MeHgCl, Ph_2S_2, Ph_3C^+, and $PhCO^+$. I is soluble in pure methanol and reacts slowly with it; this reaction is very rapid in the presence of MeO^-, but does not take place at all in the presence of H^+. I does not react with trialkyloxonium salts, noncoordinating mineral acids, O_2, Ph_3PO, $BiPh_3$, or Ph_2C_2. Many of the above reactions are being investigated further. In addition, the solid-state structures of several of the aryldiazo complexes discussed here are under study. We anticipate that the synthetic and structural chemistry of these compounds will prove to be diverse and interesting.

Acknowledgments. This research was supported by the Advanced Research Projects Agency of the Department of Defense and by the National Science Foundation through the Northwestern University Materials Research Center. We wish to thank Matthey Bishop, Inc. for the generous loan of iridium.

[8] J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc. A*, 604 (1967); J. P. Collman and C. T. Sears, *Inorg. Chem.*, **7**, 27 (1968).

Barry L. Haymore, James A. Ibers*
Department of Chemistry and Materials Research Center
Northwestern University
Evanston, Illinois 60201

Received February 5, 1973

Absolute Rate Constants for the Reaction of *tert*-Butylperoxy Radicals with Some Meta- and Para-Substituted Toluenes[1]

Sir:

We have previously shown[2] that absolute rate constants for the abstraction of a hydrogen atom from a variety of organic compounds (RH) by a tertiary peroxy radical (t-ROO·)

$$t\text{-ROO}\cdot + \text{RH} \xrightarrow{k_p} t\text{-ROOH} + \text{R}\cdot \qquad (1)$$

can be described by eq 2. This implies that the reac-

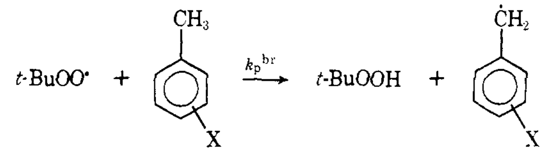
$$\log\,[k_p/(M^{-1}\ \text{sec}^{-1})] = 15.4 - 0.2D[\text{R–H}] \qquad (2)$$

tivity of R–H to a particular peroxy radical is governed principally by the strength of the weakest bond in RH, D[R–H].

It has, however, been suggested[3,4] that polar effects may play an important role in determining the reactivity of some substrates. For example, the existence of Hammett $\rho\sigma$ or Brown $\rho\sigma^+$ correlations, with negative ρ values, for meta- and para-substituted toluenes and cumenes has been cited as evidence for the contribution of dipolar structures, such as $ROO^{\delta-}:H\cdot^{\delta+}CH_2C_6H_4X$, to the transition state.

The concept of polar effects in H-atom transfer reactions has recently been questioned by Zavitsas and Pinto[5] because of a linear correlation that was obtained between ρ and ΔH for the abstraction of a hydrogen atom from ring-substituted toluenes by Cl·, Br·, t-BuO·, Cl_3C·, and C_6H_5. These workers concluded that ρ depends only on the extent of bond breaking as reflected by ΔH and that differences in the relative reactivities of substituted toluenes to a particular radical are due to differences in D[R–H].

We now report absolute rate constants for the reaction of 13 ring-substituted toluenes with *tert*-butylperoxy radicals in an attempt to determine the importance of polar effects on the H-atom transfer reaction



(3)

Table I. Absolute Rate Constants for the Reaction of Some Para- and Meta-Substituted Toluenes with *tert*-Butylperoxy Radicals at 30°

Substituent	k_p^{br}, M^{-1} sec^{-1} [a]
p-Methoxy[b]	0.083
p-Phenoxy	0.066
p-Methyl	0.056
m-Methyl	0.035
None	0.031
p-Chloro	0.030
m-Methoxy[b]	0.027
p-Carbomethoxy	0.025
m-Chloro	0.018$_5$
p-Cyano	0.014
p-Nitro	0.014$_5$
m-Cyano	0.011
m-Nitro	0.010$_5$
p-Acetyl	0.008

[a] Overall propagation rate constant, the values for *p*- and *m*-xylene were statistically corrected. [b] Values of k_p^{br} (overall) = 0.0025 and 0.0035 M^{-1} sec^{-1} were found for anisole and *p*-methoxyanisole, respectively. The k_p^{br} values of *p*-methoxytoluene and *m*-methoxytoluene have been corrected for this contribution.

These rate constants were determined by the "hydroperoxide method" described in previous papers in this series[6] and are listed in Table I. Plots of log (k_p^{br}/M^{-1} sec^{-1}) against Hammett σ or Brown σ^+ substituent

---

[1] (a) Absolute Rate Constants for Hydrocarbon Autoxidation. XXIII. (b) Issued as NRCC No. 13198.

[2] S. Korcek, J. H. B. Chenier, J. A. Howard, and K. U. Ingold, *Can. J. Chem.*, **50**, 2285 (1972).

[3] (a) G. A. Russell, *J. Amer. Chem. Soc.*, **78**, 1047 (1956); (b) G. A. Russell and R. C. Williamson, Jr., *ibid.*, **86**, 2357 (1964).

[4] J. A. Howard, K. U. Ingold, and M. Symonds, *Can. J. Chem.*, **46**, 1017 (1968).

[5] A. A. Zavitsas and J. A. Pinto, *J. Amer. Chem. Soc.*, **94**, 7390 (1972).

[6] See ref 2 and references listed therein.

constants[7,8] yielded the correlations: log $(k_p^{br}/M^{-1}\ \text{sec}^{-1}) = -0.78\sigma - 1.4$ $(r = -0.93)$ and log $(k_p^{br}/M^{-1}\ \text{sec}^{-1}) = -0.56\sigma^+ - 1.5$ $(r = -0.97)$, 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 $D[p\text{-}CH_3OC_6H_4CH_2\text{–}H]$ and $D[p\text{-}NO_2C_6H_4CH_2\text{–}H]$, 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 $(k_p^{br}/M^{-1}\ \text{sec}^{-1}) = -0.76\sigma_m - 1.49$ $(r = 0.99)$. 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.

---

(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 $(k_p^{br}/M^{-1}\ \text{sec}^{-1}) = -0.61(\sigma^0 + 0.77\Delta\bar{\sigma}_R^+) - 1.47$ $(r = -0.98)$, 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.

J. A. Howard*, J. H. B. Chenier
Division of Chemistry, National Research Council
Ottawa, Ontario, Canada

Received December 6, 1972

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-

---

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