Extension of Structure-Reactivity Correlations for the Hydrogen Abstraction Reaction to Bromine Atom and Comparison to Chlorine Atom and Hydroxyl Radical

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ABSTRACT

Recently we presented structure-reactivity correlations for the gas-phase ambient-temperature rate constants for hydrogen abstraction from sp^3-hybridized carbon by chlorine atom and hydroxyl radical (Cl•/HO• + HCR_3 → HCl/HOH + •CR_3); the reaction enthalpy effect was represented by the independent variable Δ_rH and the "polar effect" by the independent variables F and R, the Hammett constants for field/inductive and resonance effects. Both these reactions are predominantly exothermic and have early transition states. Here we present a parallel treatment for Br• whose reaction is significantly endothermic with a correspondingly late transition state. In spite of lower expectations because the available data base is less extensive and much more scattered and because long temperature extrapolations are often required, the resulting least-squares fit ($\log k_{298,Br} = -0.147\ \Delta_rH - 4.32\ \Sigma F - 4.28\ \Sigma R - 12.38$ with $r^2 = 0.92$) was modestly successful and useful for initial predictions. The coefficient of Δ_rH was ≈4-fold greater, indicative of the change from an early to a late transition state; meanwhile the sizable coefficients of ΣF and ΣR indicate the persistence of the "polar effect". Although the mean unsigned deviation of 0.79 log k_{298} units is rather large, it must be considered in the context of a total span of over 15 log units in the data set. The major outliers are briefly discussed.

INTRODUCTION

We recently proposed empirical correlations based on a linear combination of independent variables for the extensive data bases of ambient-temperature gas-phase site-specific rate constants for hydrogen atom abstraction from sp^3-hydridized carbon centers (HCR_3) by Cl•[1] and HO•.[2] These reactions are almost always exothermic as dictated by the strong bond dissociation energies of the products: BDE(H—Cl) = 431.4 kJ/mol and BDE(H—OH) = 497.3 kJ/mol. We explore herein the same approach for abstractions by Br• which, by contrast, are almost always endothermic because of the much weaker HBr bond formed (BDE(H—Br) = 366.2 kJ/mol). These previous correlations are shown as eqns 1 and 2 as the slightly truncated forms in which a minor term in Δ_rH^2 has been dropped.[2] Such hydrogen atom transfer has long been known to be facilitated by substituents R that increase the radical stability and hence the exothermicity

$$H—CR_3 + Cl• \ (HO•) \ (Br•) \rightarrow •CR_3 + HCl \ (HOH) \ (HBr)$$

$$\log k_{298,Cl} = -0.0347 \ \Delta_rH - 3.239 \ \Sigma F - 2.201 \ \Sigma R - 12.34 \qquad (1)$$

$$\log k_{298,OH} = -0.0424 \ \Delta_rH - 1.021 \ \Sigma F - 0.965 \ \Sigma R - 16.76 \qquad (2)$$

of the reaction and also by those that stabilize the development of a partial positive charge at the developing carbon radical center in the transition state.[3-5] For a recent instructive example of this interplay of thermochemistry and polar effects ($^{\delta-}X---H---R^{\delta+}$) as a function of the attacking radical, see the computational results for hydrogen abstraction from model acetylated amino acids.[6-7] Our particular choice of the independent variables, Δ_rH and the Hammett constants and to represent these enthalpic and polar effects, was influenced by their availability for a large variety of substituents. The Δ_rH term represents the enthalpy effect in the spirit of the Evans-Polanyi

relationship; the ΣF term, the sum of the Hammett F parameters for the three substituents on carbon, addresses the σ-field/(inductive) effect on the polar transition state, and the ΣR term, the corresponding sum of the Hammett R parameters, addresses the parallel π-resonance effect.[8] Note that $(\sigma_F + \sigma_R) = \sigma_{para}$. To transform the coefficient of the $\Delta_r H$ term into an approximate analog of the Evans-Polanyi α coefficient (the historical formulation involved the activation energy rather than the rate constant, i.e., $E = \alpha\ \Delta_r H + E^0$), we define α' = (coefficient of $\Delta_r H$)(2.303RT) and obtained $\alpha'_{Cl} = 0.20$ and $\alpha'_{OH} = 0.24$, values significantly <0.5 and hence consistent with an early transition state for both cases, as anticipated.

EXPERIMENTAL DATA BASE

The data base of experimental gas-phase rate constants k_{Br} is less extensive and less internally consistent than those for k_{Cl} or k_{OH}, nor do we have the advantage of a compilation of evaluated and recommended values as we had for k_{Cl}[1] and k_{OH}.[2] In addition, because of the lower reactivity of Br•, Arrhenius parameters have typically been obtained at higher temperature and therefore require longer, and questionable, extrapolations to 298 K. A compilation is given in Table 1.[9-53] All formulas have the carbon from which hydrogen abstraction occurs at the beginning followed by the substituents attached, i.e., CH_3X, CH_2XY, or CHXYZ. For compounds with multiple potential abstraction sites, the experimental rate constant is typically assumed to be dominantly that of the most reactive site, a relatively safe assumption (see below) given the known high selectivity of Br•, compared with, for example, Cl•. All A values (per molecule) and k_{298} values (corrected to a per reactive hydrogen basis) are in units of

cc/molecule-s. All $\Delta_r H$ and E values are in units of kJ/mol. For internal consistency, the $\Delta_r H$ values are based on the same

Table 1 Data, Experimental Methods, and Variations from Correlation for Hydrogen Abstraction by Br•[a]

Compound	T range	A	E	log k_{298}[b]	$\Delta_r H$	ΣF[c]	ΔR[c]	Δlog k_{298}[d]	Method[e]	Ref
										10
CH_4	298-478	5.00E–10	73.9	–22.86	72.8	0.00	0.00	0.23	Rel to CH_3CHF_2 (ref 9), then to C_2H_6 (ref 9), then to C_3H_8 (ref 10), and then to *i*-C_4H_{10} (ref 10); Abs-F ref (11)	12
CH_4	≈600	1.63E–10	77.7	–24.02	72.8	0.00	0.00	–0.93	Rel to CF_3H (ref 9); Abs-T (ref 9); for a recent summary see ref 13	9
CH_3CH_3	473-621	2.35E–10	53.3	–19.75	55.9	0.01	–0.18	0.12	Abs-F (ref 14)	14
CH_3CH_3	494-592	6.61E–10	58.6	–20.23	55.9	0.01	–0.18	–0.35	Abs-T (ref 15)	15
CH_3CH_3	≈600	2.27E–10	57.2	–20.44	55.9	0.01	–0.18	–0.57	Rel to CF_3H (ref 9); Abs-T (ref 9)	9
CH_3CH_3	298-478	7.00E–10	53.4	–19.29	55.9	0.01	–0.18	0.58	Rel to C_3H_8 (ref 10) and then to *i*-C_4H_{10} (ref 10); Abs-F (ref 11)	12
CH_3CH_3	310	7.00E–10	55.0	–19.57	55.9	0.01	–0.18	0.30	Rel to CH_2ClBr (ref 16); Abs-F (ref 17) AND Rel to $CH_3C(CH_3)_3$ (ref 16); Abs-F (ref 18); reported k_{310}; adjusted to k_{298} assuming E = 55	16
$CH_3C(CH_3)_3$	688-775	1.14E-9	57.6	–20.12	53.3	–0.02	–0.18	–0.76	Abs-F (18)	18
$CH_3C(CH_3)_3$	298			–20.13	53.3	–0.02	–0.18	–0.77	Rel to C_2H_6 (ref 19); Abs-F (ref 13)	19
$CH_3C(CH_3)_3$	≈600	5.06E-10	60.5	–20.98	53.3	–0.02	–0.18	–1.62	Rel to CF_3H and C_2F_5H (ref 9); Abs-T (ref 9)	9
$CH_3CH=CH_2$	273-318	8.15E-13	10.4	–14.39	2.3	0.13	–0.17	–1.84	Abs-F (ref 20); followed formation of HF; upper limit if an addition-elimination channel also gives HF	20
E-$CH_3CH=CHCH_3$	233-320	5.80E-12	8.0	–13.41	–2.7[f]	0.09	–0.18	–1.82	Abs-F (ref 21); followed formation of HF; upper limit if an addition-elimination channel also gives HF	21
$(CH_3)_2C=C(CH_3)_2$	233-320	2.40E-11	0.6	–11.81	–7.7[f]	0.05[f]	–0.19[f]	–1.16	Abs-F (ref 22); followed formation	22

									of HF; upper limit if an addition-elimination channel also gives HF	
$(CH_3)_2C=C(CH_3)_2$	274-420	3.84E-11	1.4	–11.74	–7.7[f]	0.05[f]	–0.19[f]	–1.10	Abs-F (ref 23); addition considered reversible under reaction conditions	23
$CH_3C_6H_5$	302-352	3.70E-12	13.6	–14.25	9.1	0.12	–0.13	–0.61	Rel to *i*-C_4H_{10} (ref 24); Abs-F (ref 14)	24
$CH_3C_6H_5$	300			–14.36	9.1	0.12	–0.13	–0.69	Rel to C_2H_5OH (ref 25), then to $(CH_3)_2CHCH(CH_3)_2$ (ref 26), and then to *i*-C_4H_{10}; Abs-F(ref 11); addition to C_6H_6 order of magnitude slower	25
CH_3CH_2F	353-423	5.63E-12	54.2	–21.23	69.3	0.15	–0.04	1.82	Rel to C_2H_5Cl and then to C_2H_6 (ref 27); Abs-F (ref 28)[g]; regiochemistry from product analysis	27
CH_3CF_3	≈600	1.70E-10	98.2	–27.45	81.6	0.38	0.16	–0.74	Rel to CF_3H and C_2F_5H (ref 9); Abs-T (ref 9)	9
CH_3CH_2Cl	343-423	6.61E-12	59.2	–22.03	56.7	0.13	–0.01	–0.79	Rel to C_2H_6 (ref 29); Abs-T (ref 9)[g]; regiochemistry from product analysis	29
CH_3CCl_3	565-694	3.31E-10	83.3	–24.55	67.7	0.38	0.09	–0.19	Abs-T on Br_2-catalyzed elimination of HCl from CH_3CCl_3 (ref 30); A_{exp} decreased by 0.5 log units	30
$CH_3C(=O)CH_3$	536-618	1.66E-10	58.2	–20.75	39.8	0.33	0.17	–0.37	Abs-T (ref 31)	31
$CH_3C(=O)CH_3$	298			–20.12	39.8	0.33	0.17	0.26	Rel to *neo*-C_5H_{12} (32); Abs-F (ref 18)	32
CH_3OH	439-713	[h]	[h]	–16.26	35.5	0.33	–0.70	–0.23	Abs-F (ref 33)	33
CH_3OH	349-408	[i]	[i]	–17.14	35.5	0.33	–0.70	–1.12	Abs-T with photo-initiation; complex kinetics with orders dependent on concentrations	34

CH_3OCH_3	300-350	3.80E-10	29.4	–15.36	37.6	0.29	–0.56	1.41	Rel to *i*-C_4H_{10} (ref 35); Abs-F (ref 14)	35
CH_3OCH_3	298			–15.58	37.6	0.29	–0.56	1.18	Rel to *i*-C_4H_{10} (ref 35); Abs-F (ref 11,14)	36
CH_3SCH_3	386-604	9.11E-11	19.9	–14.31	25.5	0.23	–0.23	1.83	Abs-F (ref 37)	37
$CH_3S(=O)CH_3$	298			–14.74	26.9	0.52	–0.03	3.72	Abs-F (discharge flow generation) (ref 38); major channel; minor channel gave CH_3•	38
CH_3F	≈600	9.04E-11	67.4	–22.33	55.2	0.45	–0.39	–1.56	Rel to CF_3H; Abs-T (ref 9)	39
CH_3Cl	≈600	1.19E-10	61.6	–21.20	51.0	0.42	–0.19	–0.32	Rel to CF_3H and C_2F_5H; Abs-T (ref 9)	39
CH_3Cl	353-423	1.16E-10	57.0	–20.47	51.0	0.42	–0.19	0.41	Rel to C_2H_6 (ref 39); Abs-F (ref 28)	40
CH_3Cl	332-473	1.30E-10	57.7	–20.48	51.0	0.42	–0.19	0.40	Rel to C_2H_6 (ref 39); Abs-F (ref 12)	41
CH_3Br	≈600	1.66E-10	68.2	–22.22	60.1	0.45	–0.22	0.00	Rel to CF_3H and C_2F_5H; Abs-T (ref 9)	39
CH_3Br	353-410	7.44E-11	62.8	–21.61	60.1	0.45	–0.22	0.61	Rel to CH_2ClBr (ref 42); Abs-F (ref 16)	42
$CH_2(CH_3)_2$	476-667	8.78E-11	36.0	–16.67	43.1	0.02	–0.36	0.59	Abs-F (ref 14)	14
$CH_2(CH_3)_2$	≈600	1.51E-10	43.6	-17.76	43.1	0.02	–0.36	–0.49	Rel to CF_3H and C_2F_5H; Abs-T (ref 9)	39
$CH_2(CH_3)_2$	298-478	4.70E-10	39.8	–16.61	43.1	0.02	–0.36	0.66	Rel to *i*-C_4H_{10} (ref 10); Abs-F (ref 11)	12
$CH_2(CH_3)(C_2H_5)$	447-625	2.86E-10	37.7	–16.75	44.3	0.01	–0.33	0.77	Abs-F (ref 14)	14
$CH_2(CH_3)(C_2H_5)$	≈300-500	8.32E-10	44.6	–17.50	44.3	0.01	–0.33	0.02	Rel to C_2H_6 (39); average of Abs-T (ref 15) and Abs-T (ref 9); regiochemistry from product analysis	43
$CH_2(CH_3)(C_2H_5)$	≈600	4.79E-10	43.9	–17.62	44.3	0.01	–0.33	–0.09	Rel to CF_3H and C_2F_5H; Abs-T (ref 9)	39
$CH_2(CH_3)OH$	300			–14.34	34.3	0.34	–0.88	0.79	Rel to $(CH_3)_2CHCH(CH_3)_2$ (ref 26)	25

									and then to *i*-C_4H_{10}; Abs-F(ref 11)	
$CH_2(CH_3)OC_2H_5$	298-333	1.05E-10	16.3	–13.44	34.3	0.30	–0.88	1.68	Abs-VLPR; A assigned	44
$CH_2(CH_3)OC_2H_5$	300-350	2.80E-10	20.3	–13.71	34.3	0.30	–0.88	1.41	Rel to *i*-C_4H_{10} (ref 35); Abs-F (ref 14)	35
$CH_2(CH_3)OH$	298			–14.34	34.3	0.34	–0.88	0.89	Rel to *i*-C_4H_{10} (ref 36); Abs-F (ref 14)	36
$CH_2(C_2H_5)OH$	298			–14.38	25.6	0.33	–0.88	–0.45	Rel to $(CH_3)_2CHCH(CH_3)_2$ (ref 26) and then to *i*-C_4H_{10}; Abs-F(ref 11)	25
$CH_2(CH_3)F$	≈600	2.19E-11	48.5	–19.46	53.2	0.46	–0.57	0.29	Rel to CF_3H and C_2F_5H; Abs-T (ref 9)	9
$CH_2(CH_3)F$	353-423	1.07E-11	43.3	–18.87	53.2	0.46	–0.57	0.88	Rel to C_2H_5Cl and then to C_2H_6 (ref 27); Abs-F (ref 28)[g]; regiochemistry from product analysis	27
$CH_2(CH_3)Cl$	313-423	8.70E-12	37.8	–17.99	40.2	0.43	–0.37	0.58	Rel to C_2H_6 (ref 29); Abs-F (ref 14)	41
$CH_2(CH_3)Cl$	313-373	8.52E-12	41.6	–18.67	40.2	0.43	–0.37	–0.10	Rel to C_2H_6 (ref 29)[g]; Abs-T (ref 9); regiochemistry from product analysis	29
$CH_2(CH_3)Cl$	305-368	2.53E-12	38.2	–18.60	40.2	0.43	–0.37	–0.03	Rel to C_2H_6 (ref 45); Abs-T (ref 9); earlier version of ref 29 without regiochemistry	45
$CH_2(CH_3)Br$	313-373	2.51E-11	47.7	–19.26	40.3	0.46	–0.40	–0.68	Rel to C_2H_6 (ref 29); Abs-T (ref 9)	29
$CH_2(CH_3)Br$	313-373	7.33E-12	44.3	–19.20	40.3	0.46	–0.40	–0.62	Rel to C_2H_5Cl; value taken from (ref 45); α-product dominant	46
$CH_2(CF_3)F$	≈600	6.41E-11	81.6	–24.80	58.8	0.83	–0.23	–1.17	Rel to CF_3H and C_2F_5H (ref 9); Abs-T (ref 9)	9
CH_2F_2	≈600	3.88E-11	69.4	–22.88	65.5	0.90	–0.78	–0.31	Rel to CF_3H and C_2F_5H (ref 9); Abs-T (ref 9)	9
CH_2FCl	382-443	1.29E-10	61.9	−20.75	25.9	1.26	−0.57	−1.55	Rel to $CHCl_3$ (ref 47); Abs-T (ref 48)	47
CH_2Cl_2	297-369	3.20E-11	47.0	−19.03	37.8	0.84	−0.38	0.90	Unknown	41

CH_2Cl_2	322-394	1.62E-11	45.4	−19.06[j]	37.8	0.84	−0.38	0.88	Rel to CH_3Cl (ref 47); Abs-T (ref 9)	47
CH_2Cl_2	353-433	1.74E-11	47.4	−19.36[j]	37.8	0.84	−0.38	0.58	Rel to $CHCl_3$ (ref 47); Abs-T (ref 48)	47
CH_2ClBr	293-785	4.65E-11	47.6	−18.98	40.4	0.87	−0.41	1.35	Abs-F (ref 17) AND Rel to $CH_3C(CH_3)_3$ (ref 16); Abs-F (ref 18)	17
$CH(CH_3)_3$	298-478	1.83E-10	28.7	−14.77	34.0	0.03	−0.54	0.43	Abs-F (ref 11)	11
$CH(CH_3)_3$	423-621	1.61E-10	28.8	−14.84	34.0	0.03	−0.54	0.35	Abs-F (ref 14,28)	14
$CH(CH_3)_3$	≈600	6.33E-11	32.5	−15.90	34.0	0.03	−0.54	−0.70	Rel to CF_3H and C_2F_5H (ref 9); Abs-T (ref 9)	39
$CH(CH_3)_3$	298			−14.35	34.0	0.03	−0.54	0.84	Abs-VLPR (ref 49)	49
$CH(CH_3)_3$	298-363	4.17E-11	28.0	−15.29	34.0	0.03	−0.54	−0.10	Abs-VLPR (ref 50); A assigned; complicated by presence of excited Br• from the entry discharge	50
$[CH(CH_3)_2]_2$	295			−14.49	34.0	0.03	−0.54	0.70	Rel to *i*-C_4H_{10} (ref 26); Abs-F (ref 11)	26
$CH(CH_3)_2OH$	300			−13.34	17.3	0.35	−1.06	−1.44	Rel to ethyne and traceable to *i*-C_4H_{10} (ref 25); Abs-F (ref 11)	25
$CH(CH_3)F_2$	≈600	3.81E-11	60.9	−21.09	53.4	0.91	−0.96	−1.04	Rel to CF_3H and C_2F_5H (ref 9); Abs-T (ref 9)	9
$CH(CH_3)Cl_2$	308-368	1.20E-12	30.9	−17.34	26.6	0.85	−0.56	0.23	Unknown	41
$CH(CH_3)Cl_2$	308-368	1.15E-12	30.5	−17.30	26.6	0.85	−0.56	0.27	Rel to CH_3CH_2Cl and then to C_2H_6 (ref 51); Abs-F (ref 28)	51
$CH(CH_3)Br_2$	308-368	3.65E-13	29.7	−17.65	30.9[f]	0.91	−0.62	0.55	Rel to C_2H_6 (ref 51); Abs-F (ref 28)	51
$CH(CHF_2)F_2$	≈600	6.63E-11	81.0	−24.67	64.6	1.19	−0.75	−0.86	Rel to CF_3H and C_2F_5H (ref 9); Abs-T (ref 9)	9
$CH(CF_3)_2F$	421-534	7.59E-12	81.2	−25.35	67.0[k]	1.19	−0.75	−1.19	Abs-T (ref 52)	52
$CH(CF_3)F_2$	596-731	1.76E-11	80.8	−24.91	68.3	1.28	−0.62	0.39	Abs-T (ref 9)	9
CHF_3	646-738	2.12E-11	93.4	−27.04	80.2	1.35	−1.17	−2.04	Abs-T (ref 9)	9
CHF_2Cl	353-423	1.06E-10	66.9	−21.70	55.4	1.32	−0.97	0.38	Rel to CH_3Cl (ref 40) and then to C_2H_6 (ref 39); Abs-F (ref 28)	40

$CHFCl_2$	371-444	1.74E-11	55.6	−20.51	37.8	1.29	−0.77	−0.30	Rel to $CHCl_3$ (ref 47); Abs-T (ref 48)	47
$CHCl_3$	420-455	3.80E-12	38.9	−18.24	25.9	1.26	−0.57	0.95	Abs-T (ref 48)	48
$CHBr_3$	588			−18.76	26.5	1.35	−0.66	0.52	Abs-T (ref 53); A and E values assigned	48

[a]T in K; A (per molecule) and k_{298} (per reactive hydrogen) in cc/molecule-s; E and Δ_rH in kJ/mol. [b]Reported experimental expression extrapolated to 298 K. [c]From ref 8. [d]$\Delta\log k_{298}$ = (experimental value) – (value from correlation). [e]Abs-T = absolute value from thermal bromination; Abs-VLPR = absolute value from VLPR; Abs-F = absolute value from flash photolysis and real-time measurement of Br• decay; Rel = relative rate constant ultimately traceable to absolute value for last compound shown; any additional bridging compounds and references; final symbol gives method and reference for the last compound in the series (see elsewhere in the Table). [f]Estimated. [g]For the absolute value of $k_{298}(C_2H_6)$, ref 27 used 1.91E-20 from ref 28 (cf. ref 12), while ref 29 used 3.62E-21 from ref 9; hence the ethyl halides are offset by a factor of 5. [h]$k = (5.66E\text{-}15)(T^{1.5})(\exp(-29.9/RT))$. [i]$k = (4.40E\text{-}14)(T^{0.5})(\exp(-25.9/RT))$. [j]Note two results by same authors differ by a factor of 2. [k]From ref 52.

$\Delta_fH(\bullet CR_3)$ values used in our previous study of Cl•,[1] i.e., $\Delta_rH_{Br} = \Delta_rH_{Cl} + [BDE(HCl) - BDE(HBr)] = \Delta_rH_{Cl} + 65.2$. (There is considerable circularity involved for Br• because many of the $\Delta_fH(\bullet CR_3)$ values have been obtained from the forward and reverse kinetics of the R• + HBr = RH + Br• equilibrium.)[54]

Three general methods have been used to obtain absolute values of rate constants: (1) the kinetics of thermal bromination from which k_{Br} can be extracted , (2) direct measurement of effusing reactive species from a Knudsen cell, i.e., the "very low pressure reactor" (VLPR), and (3) flash photolysis pulsed systems in which the decay of Br• can be followed directly by rapid spectroscopic techniques. Determination of the experimental rate constant for a radical chain reaction with alternating propagation steps and radical-combination termination steps typically gives a composite $k_{exp} = k_{propagation}(k_{initiation}/k_{termination})^{1/2}$ in which the rate-controlling $k_{propagation}$ value is convoluted with $k_{initiation}$ and $k_{termination}$, both of which must be measured or estimated from additional sources. However for thermal bromination, if concentrations are adjusted such that $k_{propagation}$ is the desired k_{Br} for hydrogen atom abstraction, then $k_{exp} = k_{Br}[K(Br_2)]^{1/2}$ where $K(Br_2)$ is the known dissociation constant for Br_2.[55] In this way, absolute measurements of k_{Br} have been reported for ethane,[15] 1,1,1-trichloroethane,[30] acetone,[31] methanol,[34] 1,1,1,2,3,3,3-heptafloropropane,[52] pentafluoroethane,[9] fluoroform,[9] chloroform,[48] and bromoform.[53] The VLPR technique, in which the Knudsen cell reactor operates as a "continuously stirred tank reactor" and the concentrations of Br• and RH are determined directly by mass spectrometry on the effusing beam, has been applied to diethyl ether[44] and *i*-butane.[49,50] However, the A value from a temperature variation study is often modified from the experimental value by statistical mechanics considerations and

hence the extrapolation to 298 K is affected. More recent methods have followed the decay of Br• in real time in an excess of RH by resonance fluorescence spectroscopy or mass spectrometry after its generation by a short flash photolysis or discharge pulse. This approach has been applied to ethane,[14] neopentane,[18] propylene,[20] *E*-2-butene,[21] 2,3-dimethyl-2-butene,[22,23] methanol,[33] dimethyl sulfide,[37] dimethyl sulfoxide,[38] propane,[14] *n*-butane,[14] bromochloromethane,[17] and *i*-butane.[11,14,28]

The remainder of the kinetic values in Table 1 are from steady-state relative rate studies in which the compound of interest competes for Br• with a reference compound whose kinetic information is available from one of the absolute rate methods; this relative rate approach may involve more than one bridging reference compound to arrive at one with absolute information. Both the absolute and relative rate methodologies have been described in greater detail in our exploration of the parallel reactions of Cl•.[1] The major difference is that the absolute data for Br• tend to be higher temperatures because of its much lower reactivity. This then leads to further ambiguity since the relative rate studies have often been performed over a lower temperature range than that at which the absolute Arrhenius parameters for the anchor compound were obtained.

For individual compounds for which k_{Br} has been reported from various sources, there is considerable scatter in the data, even between absolute measurements. This probably results both from imprecision in the actual measurements and from ambiguities from the long extrapolations from higher temperatures to 298 K. For example, there is a 14-fold spread in 5 extrapolated values for the common anchor ethane, including a 3-fold difference in the absolute values from the thermal bromination and flash photolysis/fluorescence detection methods. Similarly there is a 7-fold spread in 3 values

for neopentane, a 14-fold spread in 3 values for propane, a 7-fold spread in 3 values for *n*-butane, a 5-fold spread in 3 values for ethyl chloride, and a 35-fold spread in 5 values for *i*-butane, including an 8-fold difference between two VLPR studies. Further variance occurs in cases where different authors perform relative rate measurements against the same reference standard but use different absolute values for that standard.

For compounds for which $k_{298,Br}$ values are available, either directly or as the reference compound in a relative rate study, from both the thermal bromination approach and the approaches that measure the real-time decay of Br•, there is a consistent trend that the values from the former are lower. As a specific example, consider two absolute determinations for ethane, one by Pilling, Gutman, and coworkers[14] using the flash photolysis/atomic resonance detection technique and a second by Benson, Golden, and coworkers[15] using the thermal bromination technique. In the range 500-600 K, the latter[15] obtained an almost 3-fold larger A value but also an over 5-fold larger E value than the former.[14] Thus the $k_{298,Br}$ value extrapolated to ambient temperature from the former study[14] was 3-folder larger than that from the latter.[15] Dobis and Benson[56] later claimed to detect curvature in the Arrhenius plot for the data of Pilling, Gutman, and coworkers[14] of the sort that an extrapolated linear plot would overestimate $k_{298,Br}$; hence they gave more credence to the lower value of Benson, Golden, and coworkers.[15] However note that this curvature, if real, would have the unusual *opposite* sense of the common occurrence where both the lowest-temperature and highest-temperature values lie above, rather than below, the linear correlation line because of tunneling at low temperature and extraneous side reactions at high temperature. In a separate study, Dobe and coworkers[16] carried out a competition between ethane and bromochloromethane at the much lower temperature of

310 K. This latter reference compound was chosen because it had given a linear Arrhenius plot over an *unusually* wide temperature range (293-785 K)[17] by a combination of flash photolysis/fluorescence data at higher temperature *and* relative rate measurements compared to neopentane at lower temperature. The resulting value of $k_{298,Br}$ for ethane was 1.5-fold *larger*, not smaller, than that from Pilling, Gutman, and coworkers[14] (see Table 1 for the slight temperature adjustment from 310K to 298 K) and hence larger still than that from Benson, Golden, and coworkers.[15]

Given such uncertainties, we see no reliable method to identify and remove inconsistencies in the k_{Br} values in Table 1 and therefore all are retained in the correlations, including multiple values for the same compound. Hence in the Figures below in which log k_{exp} is plotted as the ordinate, the diads, triads, and even pentads of points that lie one above the other in a vertical direction represent different reported k_{exp} values for the same compound. Table 1 thus contains 78 values for 46 individual compounds. Unfortunately certain structural classes are notably missing; for example, we are unaware of kinetic data for esters. The line with unit slope shown in the Figures is the ideal 1:1 correspondence between log k_{exp} and log k_{calcd}. Hence points above this line are more reactive than predicted by the best-fit correlation while those below react more slowly. The correlation indicators used are the least-squares r^2 and the mean unsigned deviation (MUD) in log k units.

A few compounds deserve additional comment. It has already been noted above that for compounds with multiple potential abstraction sites, the experimental rate constant is assumed to be that of the most reactive site. For example, the ratio of the average total observed rate constants for ethane, propane, and *i*-butane is 1:7,600:78,000

and hence it is safe to equate them with $k_{prim,}$ k_{sec}, and k_{tert}. Only for ethyl fluoride[27] and ethyl chloride[29] have the regiochemistries (α:β = 140 and 6600, respectively) been obtained from product analysis and incorporated into the reported rate constants; for ethyl bromide[36] the dominance of the α-channel has also been demonstrated. For 1,1-dichloroethane,[41,51] k_{exp} is 230-fold greater than that for ethane, again indicative of dominant α attack. For olefins addition is more rapid than abstraction but the rate constant for abstraction has been separated out by measuring the real-time formation of HBr[20,21] or by working at high enough temperature and/or low enough pressure[23] that the addition channel is totally reversed and hence does not consume Br•. (These approaches may still give only an upper limit because of a competing addition-elimination channel.[57]) One measurement for toluene[25] gave a rate constant 10-fold larger than that for benzene under the same conditions and hence was identified largely with the abstraction channel. For dimethyl sulfoxide a minor displacement channel on sulfur was detected from product analysis and thus not included in the reported k_{Br} value.[38]

CORRELATIONS

Evans-Polanyi Treatment The modified Evans-Polanyi correlation (note that using log k rather than E as the dependent variable makes the implicit assumption that A is constant) is shown in Figure 1 and eqn 3. Some degree of correlation would be

$$\log k_{298,Br} = -0.166\ \Delta_rH - 11.62 \qquad r^2 = 0.73;\ MUD = 1.58 \qquad (3)$$

expected if for no other reason than that, as noted above, several of the Δ_rH values are based on Δ_fH values for the radicals derived from studies of the bromination equilibrium. However, the correlation indicators are modest, and the need to include a polarity

dependence is obvious. In any case, the value of $\alpha' = -0.166(2.303RT) = 0.95$ from eqn 3 is clearly indicative of the anticipated late transition state.

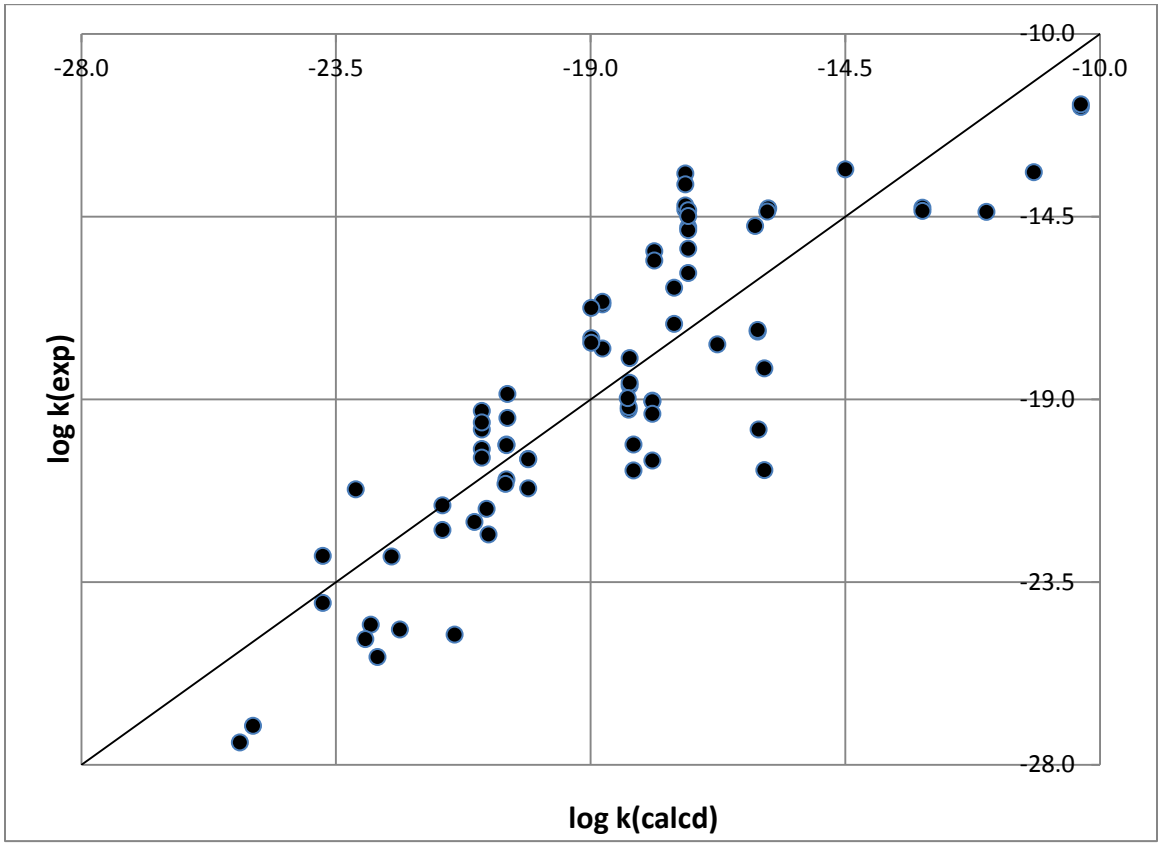

Figure 1. Evans-Polanyi plot of data in Table 1

Hammett Treatment For Cl• a correlation with Hammett constants was actually slightly better than one with $\Delta_r H$.[1] We show in Figure 2 and eqn 4 the parallel treatment for Br•. In this case the correlation was very much poorer.

$$\log k_{298,Br} = -6.04\,\Sigma F - 6.17\,\Sigma R - 18.66 \qquad r^2 = 0.39;\ MUD = 2.23 \qquad (4)$$

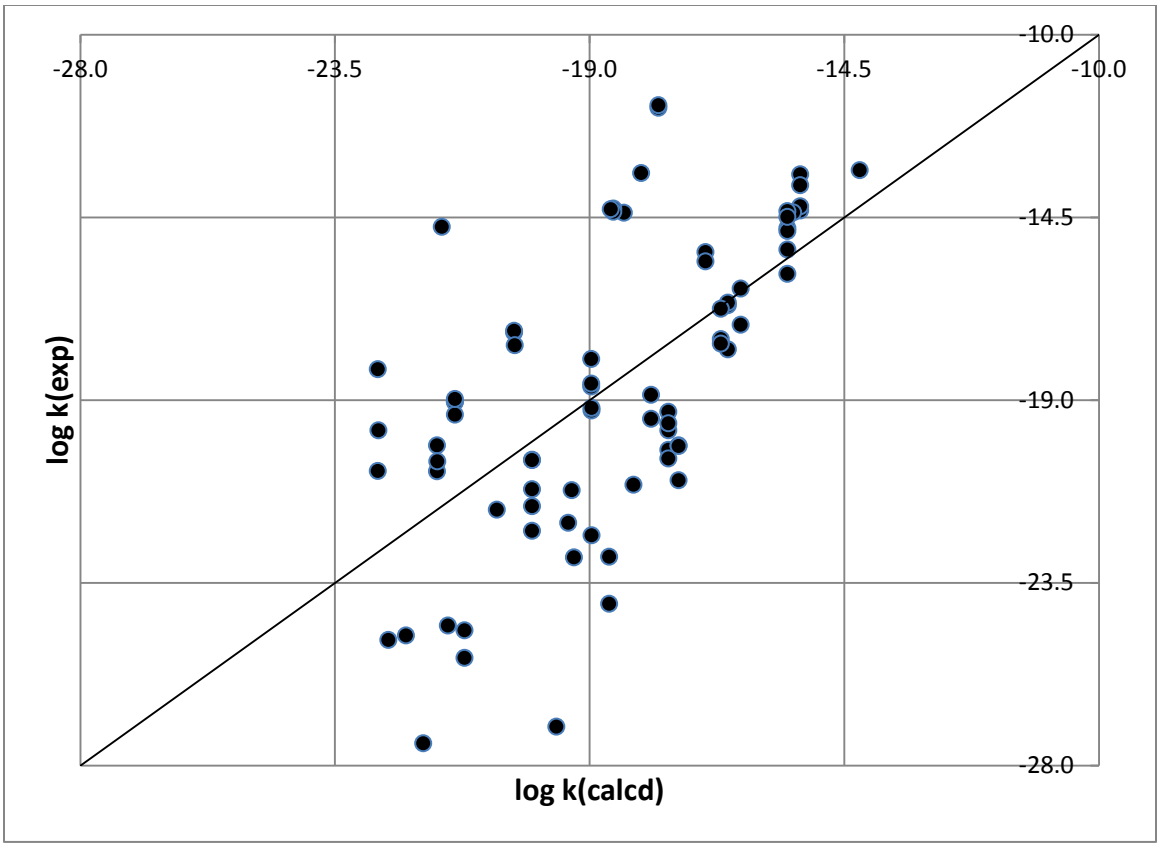

Figure 2. Hammett plot of data in Table 1

Combined Evans-Polanyi and Hammett Treatment Following the lead of eqns 1 and 2,[1,2] we finally show in Figure 3 and eqn 5 a plot in which the Evans-Polanyi and Hammett independent variables are combined. The considerable improvement

$$\log k_{298,Br} = -0.147\ \Delta_r H - 4.32\ \Sigma F - 4.28\ \Sigma R - 12.38$$

$$r^2 = 0.92;\ MUD = 0.79 \qquad (5)$$

in the correlation indicators is apparent and thus demonstrates the utility of this multi-variable approach to correlating radical abstraction reactivity for cases with late (α' = 0.84) as well as early transition states. Note that the coefficients for the Hammett terms are larger than those for either Cl• or HO•, indicative of the persistence of a significant polar effect, even though the electron affinity of Br• (3.36) is slightly less than that of Cl• (3.61 eV).[58]

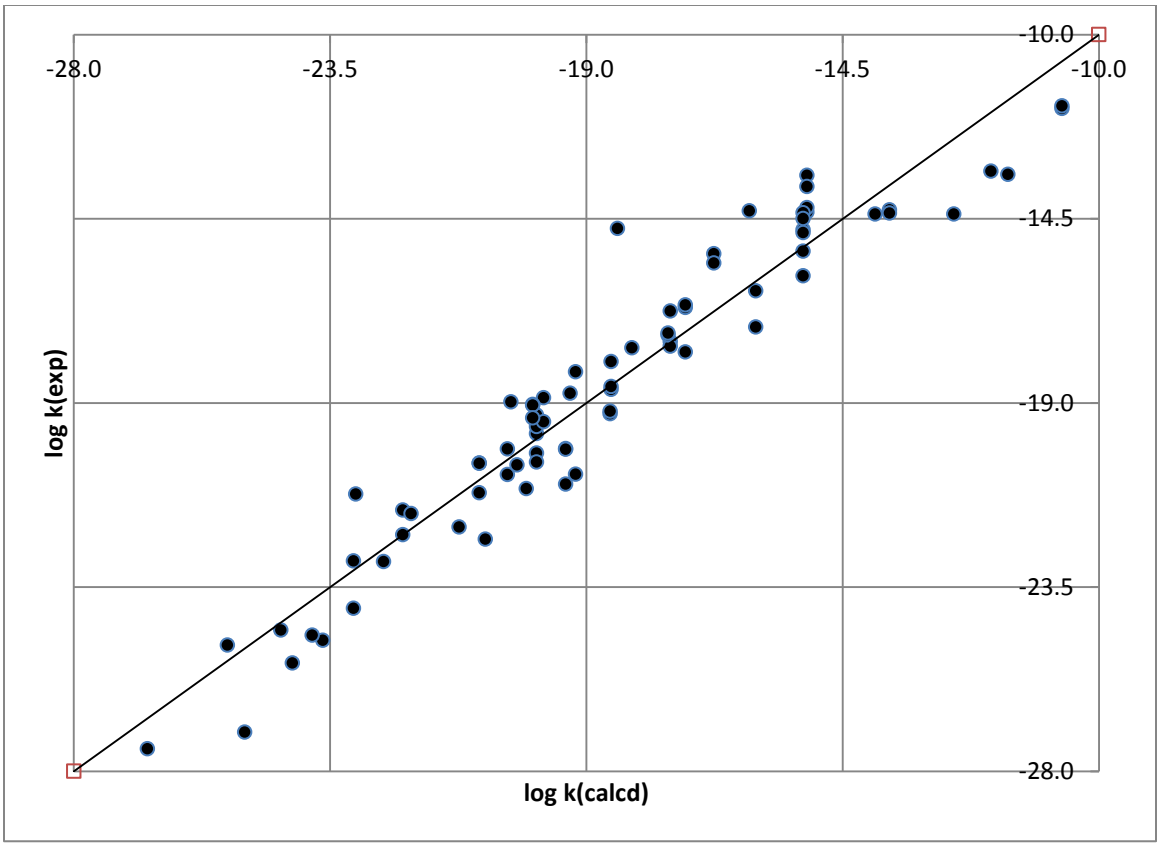

Figure 3. Combined Evans-Polanyi and Hammett plot of data in Table 1

Sensitivity Analysis The total spread in log $k_{298,Br}$ is over 15 log units from CH_3CF_3 to $CH_3(CH_3)C{=}C(CH_3)_2$, whereas that for Cl• was less than 7 log units[1] and that for HO• was only 4 log units,[2] *the compression being in the same order as the decreasing value of* $\Delta_r H$ *and the decreasing coefficients of the Hammett terms.* Thus we would expect the coefficients of the three independent variables in the best fit of eqn (5) to be greater than those in eqns (1) and (2), as is indeed true. For the $\Delta_r H$ term, a variance of ≈±1 kcal/mol (4.2 kJ/mol) would not be surprising for many of the substrates considered. This would correspond to (0.147)(4.2) = 0.62 log k units, whereas the same variances for Cl• and HO• would produce changes of only 0.15 and 0.18 log k units. Similarly, a variance of ±0.05 in ΣF would lead to changes of 0.22, 0.16, and 0.05 log k for Br•, Cl•, and HO•, respectively. A variance of ±0.05 in ΣR would lead to changes of 0.21, 0.11, and 0.05 log

k for Br•, Cl•, and HO•, respectively. Thus there is a greater sensitivity of reactivity of the endothermic late-transition-state Br• case to changes in structure compared with the exothermic early-transition-state Cl• and HO• cases. The difference is compounded by the fact that the variances in the data base for the latter are greater (see above) than the former. Hence the modestly greater MUD value for Br• (0.79) than for Cl• (0.63) or HO• (0.32) is not unexpected.

Outliers The extreme outlier with $\Delta\log k = 3.72$, i.e., the observed rate is almost four orders of magnitude larger than the correlation predicts, is $CH_3S(=O)CH_3$, even after correction for a minor channel than produces CH_3•.[38] Such a large deviation suggests a need for further data and/or improved independent variables. The remaining 7 cases with $\Delta\log k > +1$ are CH_3SCH_3 (1.83),[37] the very minor β-channel in CH_3CH_2F (1.82),[27] 2 of the 3 values for $CH_2(CH_3)OC_2H_5$ (1.68)[44] and (1.41),[35] both values for CH_3OCH_3 (1.41)[35] and (1.18),[36] and CH_2ClBr (1.35).[17] The major similar grouping is thus the simple ethers, CH_3OCH_3 and $CH_2(CH_3)OC_2H_5$, and one is tempted to suggest that the correlation does not properly address the structural feature of an -OR substituent at the radical center. However, this hypothesis is suspect because 4 of the 5 $\Delta\log k$ values for alcohols with the very similar –OH substituent at the radical center are *negative*: CH_3OH (–1.12 and –0.23),[33,34] $CH_2(CH_2CH_3)OH$ (–0.45)[25], and $CH(CH_3)_2OH$ (–1.44).[25]

The 13 cases with $\Delta\log k < -1$, i.e., the correlation over-predicts the observed value, are CHF_3 (−2.04),[9] $CH_3CH=CH_2$ (−1.84),[20] $CH_3CH=CHCH_3$ (−1.82),[21] 1 of the 3 values for $CH_3C(CH_3)_3$ (−1.62),[9] CH_3F (−1.56),[9] CH_2FCl (−1.55),[47] $CH_2(CH_3)_2OH$ (−1.44),[25] $CH(CF_3)_2F$ (−1.19),[52] $CH_2(CF_3)F$ (−1.17),[9] both values for $(CH_3)_2C=C(CH_3)_2$ (−1.16)[22] and (−1.10),[23] 1 of the 2 values for CH_3OH (−1.12),[34] and $CH(CH_3)F_2$ (−1.04).[9]

The allylic hydrogens in all four values for olefins fall into this class, suggestive of an improper treatment of this minor abstraction channel compared with olefin addition or use of a $\Delta_r H$ value that is too large. (Note that the values for $CH_3C_6H_5$ (–0.69[25] and –0.61[24]) are also negative but less dramatically so.) The second prevalent class is six fluorinated alkanes having both α- and β-F substituents; however, of the remaining values for fluorine-containing substrates, four have $-1 < \Delta\log k < 0$ and another four have $\Delta\log k > 0$. Several of the more negative cases are intertwined from a series of studies by Whittle and coworkers[9] and anchored to their absolute thermal bromination studies of CHF_3 and $CH(CF_3)F_2$.

CONCLUSION

The accuracy of any structure-reactivity correlation for hydrogen abstraction by Br• will be somewhat limited by the considerable scatter in the available data base, with three methods available for determination of absolute rate constants and with multiple values reported for the same compound. Nevertheless the "classical physical organic" treatment shown in eqn 5 again proves quite successful. The addition of Hammett constants as independent variables to represent electron withdrawal from/donation to the polar transition state gives a significant improvement over use of the Evans-Polanyi formalism alone. The larger coefficient for the $\Delta_r H$ term for Br• compared with Cl• (eqn 1) or HO• (eqn 2) is consistent with the contrast between an endothermic reaction with a late transition state and exothermic reactions with early transition states.

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TOC GRAPHIC

$Br\bullet + HCR_3 \rightarrow HBr + CR_3\bullet$

$\log k_{298} = f(\Delta_r H, \Sigma \text{ Hammett F}, \Sigma \text{ Hammett R})$

$n = 46$; $r^2 = 0.92$; MUD = 0.79 log units