excess of **3**-$d_2$ afforded an analogous 3:2 mixture of **5**-$d_0$:**5**-$d_2$. Despite complications by trace dirhenium containing impurities in this region of the spectrum that arose from the heteronuclear fragment **6**,[23] it was clear that the crossover components were significant. Furthermore, because of the statistical bias imparted by the 50-fold excess, the noncrossover components were significant.

**Photolyses of Chelate 2.** A solution of **2** (30 mg) in toluene-$d_8$ (0.40 mL) was placed in a 5-mm NMR tube along with a capillary containing a $PCl_3$ internal $^{31}P$ NMR standard. The tube was sealed under vacuum, placed in a thermostatically controlled acetone bath, and photolyzed with a 250-W sunlamp. The photolyses at 32 °C were thermally quenched at −78 °C to prevent thermal isomerizations back to starting material **2**. The $^{31}P$ NMR spectra were recorded without letting the sample warm above −78 °C. Further details of the experiments are described in the Results section.

**Acknowledgment.** We thank Dr. Alfred Bader and the Eli Lilly Co. for generous financial support of this work. We also thank P. T. Wolczanski, K. Theopold, B. K. Carpenter, C. F. Wilcox, F. Liotta, and M. Heinecky (Yale University) for helpful discussions. We are deeply indebted to S. E. Denmark, K. L. Rinehart, J. C. Cook, and R. Milberg of the University of Illinois for invaluable assistance with the mass spectroscopic analyses. Acknowledgment is made to the National Science Foundation Instrumentation Program (CHE 7904825 and PCM 8018643) for support of the Cornell Nuclear Magnetic Resonance Facility.

**Registry No. 1**, 94843-07-9; **2**, 101032-90-0; **3**, 101032-91-1; **4**, 101032-92-2; **5**, 101032-93-3; **6**, 101032-94-4; **9**, 101032-95-5; **10**, 101032-96-6; Re, 7440-15-5; Mn, 7439-96-5.

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# Temperature Dependence of the Homolytic Abstraction of Benzylic Hydrogen by Bromine Atom

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*Received August 5, 1985*

**Abstract:** The abstraction of benzylic hydrogen by bromine atom from toluene and 4-chlorotoluene has been studied by measuring the relative rates at 45.0, 25.0 10.0, 0.0, −18.5, −32.0, and −50.0 °C. The rates of 3-chloro-, 4-bromo-, 4-methyl-, and 4-nitrotoluenes relative to toluene were determined at −50.0 °C. A peculiar Arrhenius plot, a change in the sign of the slope, was observed. A Hammett plot with a $\rho$ value of −0.376 was obtained at the low temperature with the better fit with $\sigma$. The results are discussed in terms of the generally accepted interpretation of the polar effect.

The most common reaction of free radicals is the abstraction of hydrogen.[1] When toluenes serve as the hydrogen donors in this reaction, a Hammett correlation is observed.[1] While some radicals give better regressions with $\sigma$ and others with $\sigma^+$, the interpretation of the "polar effect", as generally accepted, was given by Russell.[2] The Hammett correlations of a number of abstracting radicals have been summarized.[3] This explanation of the polar effect rests upon the idea of stabilization of the transition-state structure by a polar canonical structure, II. This

$$ArCH_3 + X \rightarrow [\underset{I}{ArCH_2H\ X} \leftrightarrow \underset{II}{ArCH_2\ H{:}X}] \rightarrow ArCH_2 + HX$$

interpretation was based upon the observation that most abstracting radicals correlate with a negative value for $\rho$ in Hammett-type plots; i.e., electron-withdrawing substituents slow the reaction.[3] This polar interpretation of substituent effects seemed strengthened by the discovery that radicals of low electronegativity, *tert*-butyl,[4] 3-heptyl,[5] and undecyl,[6] afforded Hammett correlations with a positive $\rho$ value.

Zavitsas and Pinto[7] proposed that charge separation in the transition state either does not occur or is an unnecessary assumption. These workers argued that the differences in reactivities of a series of substituted toluenes toward a radical were due to differences in the bond dissociation energies, BDE, of the benzylic C–H bonds in each of the substrates. This argument depends upon the assumption that electron-withdrawing substituents increase the BDE and was based upon the observation of only negative values of $\rho$ for several abstracting radicals. This proposition was questioned by the finding of positive values of $\rho$ for abstraction reactions.[4-6] The Pryor group concluded that both the polar effect upon the transition state and upon bond dissociation energies must be considered.[8]

More recently, Dust and Arnold have presented a $\sigma\cdot$ scale based upon benzylic $\alpha$-hydrogen electron-spin resonance hyperfine coupling constants.[9] This work reexamined a series of radical reactions using an extended Hammett relation to attempt to assess the relative importance of spin delocalization (radical stabilization) vs. polar effects in radical reactions. They concluded that polar effects were dominant in the bromine atom abstraction of hydrogen from substituted toluenes. Recently it was reported[10] that this reaction has a "two-point" isokinetic temperature[10,11] of 276 K in benzene solution, a result consistent with an entropic, not an enthalpic, interpretation.

It is interesting to note that only one study has examined the role of temperature upon the homolytic polar effect as revealed by using linear free-energy relationships.[12] These workers reported that bromination using *N*-bromosuccinimide was best fit when using $\sigma^+$ from 10 to 80 °C. Their results may be extrapolated to give an isokinetic temperature of about −80 °C, and they reported that 4-chlorotoluene did not fit their otherwise "excellent" isokinetic relationship.

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**Table I.** Effect of Temperature on Relative Rates of Bromination of 4-Chlorotoluene, $k_x$, and Toluene, $k_0$

| $T$, °C | solvent | no. of expts | $k_x/k_0$ |
|---|---|---|---|
| 45 | $CCl_4$ | 3 | 0.736 ± 0.007 |
| 25 | $CCl_4$ | 2 | 0.780 ± 0.015 |
| 10 | $CFCl_3$ | 2 | 0.823 ± 0.017 |
| 0 | $CCl_4$ | 2 | 0.865 ± 0.003 |
| 0 | $CFCl_3$ | 4 | 0.866 ± 0.054 |
| -19 | $CFCl_3$ | 3 | 0.939 ± 0.001 |
| -32 | $CFCl_3$ | 3 | 0.985 ± 0.015 |
| -42 | $CFCl_3$ | 3 | 0.793 ± 0.027 |
| -50 | $CFCl_3$ | 2 | 0.759 ± 0.020 |

## Experimental Section

**Chemicals.** All reagents were obtained as Reagent Grade and were distilled through a 20-in. Vigreux column and collected as constant boiling heat cuts except for Freon 11, 99%+, and 1,2-epoxybutane which were obtained from Aldrich Chemical Co. and used as supplied and 4-nitrotoluene which was purified by crystallization from ethanol.

**Procedure.** A flask containing toluene and a substituted toluene, each ca. 0.5 M in Freon (1.0 M in carbon tetrachloride), 0.375 M chlorobenzene, as internal standard, in Freon (0.75 M $CCl_4$), and enough 1,2-epoxybutane to give at least a 3:1 molar excess over the total amount of bromine to be added was placed in a constant-temperature bath for 20 min, and nitrogen was bubbled through the solution to degas it. The epoxide was used to absorb HBr as it was generated.[13] An appropriate solution of 0.67 M bromine was then added via a pressure-equalizing funnel, and the solution was irradiated with a 275-W Sylvania sunlamp, placed externally, until all bromine was consumed as shown by the KI-starch test. The solution was agitated during the addition by the slowly bubbling nitrogen, and the bromine solution was added at a slow rate so that the reaction remained nearly colorless. The total toluenes to bromine ratio was never less than 3:1.

For temperature control above 0 °C, a large water bath with a Hakke temperature control kept the temperature within 0.1 °C. A 2-L Dewar flask was used for the lower temperatures using distilled water-ice for 0 °C, a salt-ice eutectic was used for -18.5 °C, and ethanol-water-dry ice mixtures were used for the lower temperatures. The temperature variation was no more than 0.5 °C for the temperatures at and above -32 °C and 1.0 °C below that temperature. Gas chromatographic analysis was carried out on a Perkin-Elmer Sigma 3B with flame ionization detection by using a 6-ft. 10% OV-101 on Chromosorb W column and a Hewlett-Packard 3392A integrating recorder. Temperature programming was used. Analysis was at least in quadruplicate with the relative rates obtained as previously described.[14] GC/MS analysis of the reaction mixture on an Hewlett-Packard 5880A GC interfaced with a 5970A mass detector with a 12.5-m cross-linked dimethylsilicone capillary column afforded no observable evidence of disubstitution or of ring addition.

## Results

The relative rates of 4-chlorotoluene, $k_x$, and of toluene, $k_0$, for the temperature range of 45 to -50 °C are given in Table I. The results given in this table follow a good Arrhenius relationship for the temperatures at and above -32 °C, eq 1, and a second, less good, relationship at and below that temperature, eq 2. The

$$\ln (k_x/k_0) = 298.14(1/T) - 1.243 \qquad r^2 = 0.998 \qquad (1)$$

$$\ln (k_x/k_0) = -791.284(1/T) + 3.242 \qquad r^2 = 0.898 \qquad (2)$$

results above -32 °C yield a differential energy of activation, $E_0^* - E_x^*$, of 0.59 kcal/mol, while those below give the value of -1.572 kcal/mol. The plot is shown in Figure 1.

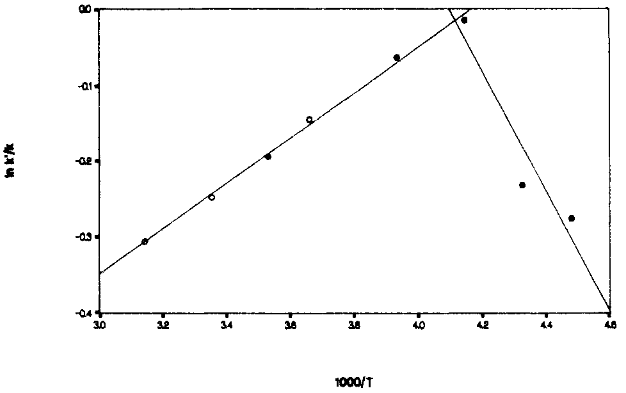

**Figure 1.** Arrhenius plot for the relative rates of 4-chlorotoluene, $k'$, and toluene, $k$.

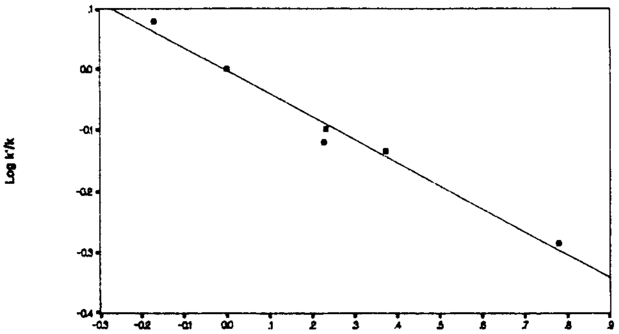

**Figure 2.** Hammett plot for the relative rates of 4-chlorotoluene, $k'$, and toluene, $k$, at -50 °C.

**Table II.** Relative Rates of Substituted Toluenes at -50 °C in $CFCl_3$ Solvent

| X | no. of expts | $k_x/k_0$ |
|---|---|---|
| H | | (1.000) |
| 3-Cl | 3 | 0.734 ± 0.028 |
| 4-Cl | 2 | 0.759 ± 0.012 |
| 4-Br | 3 | 0.806 ± 0.026 |
| 4-Me | 3 | 1.198 ± 0.042 |
| $4-NO_2$ | 2 | 0.520 ± 0.083 |

The rates of 3-chloro-, 4-chloro-, 4-bromo-, 4-methyl-, and 4-nitrotoluenes, relative to toluene, were determined at -50.0 °C to examine the Hammett relationship at this low temperature. These results are given in Table II. These results afford a Hammett relationship that is somewhat better for $\sigma$, eq 3, than for $\sigma^+$, eq 4, even thought there are too few points to be certain

$$\rho = -0.376\sigma - 0.002 \qquad r^2 = 0.980 \qquad (3)$$

$$\rho = -0.322\sigma^+ - 0.031 \qquad r^2 = 0.940 \qquad (4)$$

of this. This result is counter to those reported by Kim et al.[12] who found that the best regression for *N*-bromosuccinimide bromination was ggiven by $\sigma^+$ above 10 °C. The plot with $\sigma$ is shown in Figure 2.

## Discussion

The results presented in Table I appear to be consistent with the results obtained by others;[10,12,15] i.e., toluene reacts faster than 4-chlorotoluene with bromine atom. The value of $E_0^* - E_x^*$ of 0.592 kcal/mol for the temperature of 45 to -32 °C is not what is normally expected by traditional chemical reasoning. Below this temperature, the differential activation energy difference of -1.572 kcal/mol is what is traditionally expected. The high-temperature result calls into question the interpretation that has been given for the polar effect in abstraction reactions[2] as well as the bond dissociation energy explanation[7] and the combination of the two ideas.[8] For these higher temperature results, an entropic effect contribution must be considered as has been suggested by us[10] and others.[12] Using transition-state theory allows calculation of the entropic effect, $S_x^* - S_0^* = -2.47$ eu. This gives a value of -33 °C for the isokinetic temperature. The low-temperature results afford a differential entropy change of 6.44 eu which leads to an isokinetic temperature of -29 °C, a result acceptably close to the high-temperature result. Clearly bromine atom does not

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obey the isokinetic relationship[11] throughout the temperature range studied, but it is important to note that all abstraction reactions have been studied[3] at temperatures well above that critical temperature obtained here.

The results given above may be compared with those obtained earlier.[10] In that study, a differential energy of activation of 0.38 kcal/mol was obtained at temperatures above the isokinetic temperature, which was obtained at 2.7 °C. Those results were obtained in benzene solution where the bromine atom is known to form a complex. The differences observed in that study and this one may well represent the stability of the complex formed with benzene.

If the isokinetic relationship was obeyed throughout the temperature range studied, the sign of $\rho$ would be expected to change upon passing through the isokinetic temperature.[11] That this does not happen is readily apparent by comparing our result at −50 °C with those of Kim et al.[12] These workers obtained negative values for $\rho$ at high temperatures as did we below the isokinetic temperature. One result that differs, however, is that those workers obtained a better fit with $\sigma^+$ while ours fit better with $\sigma$, although our fit is somewhat questionable due to the use of only six points; the small value for the difference in the values of $r^2$ of 0.98 and 0.94 is only marginal. Another point of difference between our work and that of Kim is the disagreement for the values obtained for the relative rate for 4-chlorotoluene. The only directly comparable result is that at 10 °C where those workers report a value of 0.5612, while our value is 0.82. Those workers suggested three reasons that their results might differ from our earlier result of 0.96 in benzene solution.[10] We wish to thank one of the referees for suggesting three other reasons: a, different chain carriers, a strong possibility at this low temperature as Kim's results were obtained by using NBS, while we used molecular bromine; b, measurements of different things; and c, poor analytical techniques. Because of the good linearity observed for the temperature dependence and the reproducibility observed by both groups, we consider the latter reason to be unlikely. Another report relevant to our results is that of Pearson and Martin.[15] These workers showed that several *N*-bromoimides and bromine gave the same $\rho$ values and that the $\rho$ values exhibited the same temperature dependence. Their results demand parallel, if not identical, enthalpies and entropies of activation for the different reactants. Their study was for the range of 80–19 °C. This seems to invalidate reason a above, at least for the higher temperature range studied. No previous study, however, predicts or invalidates the observation of a maximum in the log $k$ vs. $1/T$ reported here.

The importance of entropy may be explained by a developing $\pi$ bond between the benzylic carbon and the ring, restricting rotation of the methyl group in the transition state. This phenomenon is predicted by MNDO calculations.[16] The importance of enthalpy may be explained by the conventional explanations.[2] It is not clear why the dramatic break in the Arrhenius plot is observed in this work. We must conclude that the reaction that was considered simple and a good model for demonstration of polar effects is not so simple and that further work must be done before we understand the mechanism of abstraction reactions. The recent explanations of Pryor[4b,c] using both bond dissociation energies and polar effects to explain the value of $\rho$ do not seem to account for the entropic effects reported in this study.

## Conclusions

The generally accepted explanations of the polar effect in hydrogen abstraction reactions are based upon enthalpic arguments. Based upon the empirical results obtained by us[10] and others[12] and the results given here for the bromination reaction, it appears that these arguments are unsatisfactory and that an entropic effect must be considered. These results raise doubts about all previous work that employed linear free-energy relationships but where the temperature effect was not studied. A typical example is that of the abstraction of iodine from substituted iodobenzenes by the 4-nitrophenyl radical where a $\rho$ value of zero was found.[17] The value of zero given in that study may be due to the reasons given, a combination of the effects of substituents upon the bond dissociation energy of the Ar–I bond and upon the stability of the transition state, or to insensitivity due to the temperature at which the study was conducted.

**Acknowledgment.** This work was funded, in part, by a grant from the Rhodes College Faculty Research and Creative Activity Committee.

**Registry No.** $H_2$, 1333-74-0; 4-chlorotoluene, 106-43-4; toluene, 108-88-3; 3-chlorotoluene, 108-41-8; 4-bromotoluene, 106-38-7; 4-methyltoluene, 106-42-3; 4-nitrotoluene, 99-99-0.

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