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Differential Activation Parameters of Rapid Atom Abstraction Reactions by Aryl Radicals. Entropy Effects in Diffusion Controlled Reactions

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Differential activation parameters for bromine atom abstraction reactions of aryl radicals in *N,N*-dimethylformamide (DMF) were determined by competition kinetics. Using H atom abstraction from DMF as the standard reaction, rate constant ratios k_H/k_{Br} were evaluated over a 40 K temperature interval. For reactions involving CBr_4, $CHBr_3$ and CH_2Br_2 the relative k_H/k_{Br} changed from 1.0 to 12.6 to 679 and from 1.0 to 7.7 to 437 when the radicals were 4-nitrophenyl and α-naphthyl, respectively. The apparent activation energies at 273 K increased in the reaction series $CHBr_3 \leq CBr_4 < CH_2Br_2$ for the abstraction of Br by both aryl radicals. The relative entropies of activation decreased in the order $CBr_4 > CHBr_3 > CH_2Br_2$ in both reactions series. It was concluded that the reactions involving CBr_4 and $CHBr_3$ are diffusion-controlled and the order of magnitude rate constant differences are due to the more negative $\Delta S^{\neq}$ when $CHBr_3$ is the bromomethane.

In connection with our work on the selectivity of aryl radicals[1,2] in the $S_{RN}1$ reaction,[3] we have examined the reactions of two different aryl radicals, 4-nitrophenyl and α-naphthyl, with bromomethanes. The objective of this work was to determine how the activation parameters for the closely related series of reactions approaching the diffusion-controlled limit depend upon the nature of the reactants. We anticipated that the reactions of the radicals with symmetrical tetrabromomethane (1), in light of other recent work,[4] could be considered to be diffusion-controlled with zero or low entropy of activation. Successive substitution of the less symmetrical bromo compounds, tribromomethane and

$$Ar^{\cdot} + CBr_4 \xrightarrow{k_1} Ar\text{-}Br + {}^{\cdot}CBr_3 \qquad (1)$$

dibromomethane, for CBr_4 was then expected to be accompanied by higher Arrhenius activation energies and more negative entropies of activation. The results reported here show that the activation energies do not vary in the anticipated manner and that the entropies of activation of these rapid reactions play a dominating role in determining the relative rates of reaction.

The abstraction of halogen atoms by free radicals has been intensively investigated.[5] The mechanism of the reaction of phenyl radicals with alkyl iodides has been convincingly demonstrated by stereochemical arguments[6] and chemically induced dynamic nuclear polarization studies[7] to involve the direct abstraction reaction without complications from the possible competing reaction, displacement by backside attack on the carbon bonded to the iodine atom. The general conclusion[5] on the mechanism of the abstraction of halogen atoms from alkyl halides is that the reactions involve cleavage of the C–X bond and the formation of the new bond in a concerted or nearly concerted manner.

RESULTS AND DISCUSSION

Diazonium salts as aryl radical sources. Aryl radicals can be generated from diazonium ions (2) either in thermal,[8] photochemical[9] or electron

$$Ar\text{-}N_2^+ + Z \rightarrow Ar^{\cdot} + N_2 + Z^+ \qquad (2)$$

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transfer[10] processes. One electron reduction produces the aryldiazenyl radical which has a very short lifetime[11] before decomposing to the aryl radical and nitrogen (3). A variety of one electron

$$\text{Ar-N}_2^+ + e^- \rightarrow |\text{Ar-N}_2^{\cdot}| \rightarrow \text{Ar}^{\cdot} + \text{N}_2 \quad (3)$$

reductants can be used to affect reaction (3), including Zn,[12] Cu powder,[13] ferrocene,[14] nitrite,[15] Cu^{I},[16] and I^-.[17] Electron transfer from pyridine has also been implicated.[18] Cathodic reduction has been developed as a source of $Ar^{\cdot}$.[19]

We have selected reaction (4)[17] as the source of aryl radicals for reactivity studies for a number of

$$\text{Ar-N}_2^+ + I^- \rightarrow \text{Ar}^{\cdot} + \tfrac{1}{2}I_2 + \text{N}_2 \quad (4)$$

reasons. The reaction is conveniently carried out simply by the mixing of stable reactants. The reaction can be affected over a wide temperature range due to the low temperature coefficient of the electron transfer process. The yield of aryl radical is essentially quantitative.[17,20] An important consideration is that the initial reaction, *i.e.* the electron transfer, is slow enough in DMF so that it takes place after mixing is complete. The latter is a very important factor when determining relative rate constants by competition techniques since in cases where the generation of the intermediate is diffusion controlled the reaction rates can be determined by the rate of mixing.[21] Under the conditions used in this study, we observe that reaction is not complete 5 min after mixing at 0 °C, eliminating any possibility of complications due to incomplete mixing.

The kinetic procedure. The aryl diazonium salt (<0.009 mmol) dissolved in *N,N*-dimethylformamide (DMF, 2.0 ml) containing the appropriate bromomethane under an atmosphere of nitrogen was allowed to come to thermal equilibrium before injecting a 100 μl aliquot of a solution of Bu_4NI (0.01 mmol) in DMF. Mixing was achieved by the pressure injection of the Bu_4NI solution while momentarily bubbling N_2 through the solution. No difference could be detected in the product ratios when the Bu_4NI solution was added dropwise. The temperature was held constant by large capacity water baths at either room temperature, 0 °C in the presence of ice or at about 40 °C by a thermostated heater. In all cases, the temperature was constant within 0.2 °C. The solution was allowed to stand for 30 min before mixing with a dilute aqueous $Na_2S_2O_3$ solution (2.0 ml) and extracting with pentane (2.0 ml). The extraction procedure was tested on known mixtures.

The pentane solutions were treated with anhydrous $MgSO_4$ to remove traces of water before GLC analysis. The GLC response factors were determined in order to convert area ratios to mol ratios of the products. The relative rate constants were calculated from eqn. (5) where k_H refers to the rate constant for abstraction of hydrogen atoms

$$k_H/k_{Br} = (A_H/A_{Br})(r_H/r_{Br})(n_{BM}/n_{DMF}) \quad (5)$$

from DMF, k_{Br} to the rate constant for abstraction of bromine atoms from the bromomethane, the A values to the appropriate product GLC areas, the r values to the response factors, and the n values to the number of mol of bromomethane and DMF present in the reaction mixtures. Eqn. (5) is valid under conditions where n_{BM} and n_{DMF} remain effectively unchanged during the reaction. The maximum change in n_{BM} occurred when the bromomethane was CBr_4 and this was always less than 5 %.

Measurement precision. The limitation in the precision of the rate constant ratios was found to be in the reproducibility of duplicate runs. Variations of the order of ±5 % in k_H/k_{Br} were observed. Since the error (r) divided by k_H/k_{Br} is small compared to unity, relationship (6) holds. The error in the differential activation energy (ΔE_a) is then expressed in (7) when the data refer to two temperatures.[22] A 5 % error in k_H/k_{Br} for a temperature interval of 273 to 313 K then corresponds to an error of ±0.2 kcal/mol in ΔE_a. The differential entropy of activation is given by (8) and the error in $\Delta\Delta S^{\neq}$ is given by (9) derived from (6) and (7).

$$\ln(k_H/k_{Br} \pm r) = \ln k_H/k_{Br} \pm r(k_{Br}/k_H) \quad (6)$$

$$\text{Error in } \Delta E_a = \pm[RT_1T_2/(T_2 - T_1)]r(k_{Br}/k_H) \quad (7)$$

$$\Delta\Delta S_T^{\neq} = R \ln(k_H/k_{Br}) + \Delta E_a/T \quad (8)$$

$$\text{Error in } \Delta\Delta S_T^{\neq} = \pm(R(r) + (\text{Error in } \Delta E_a)/T) \quad (9)$$

Thus a 5 % error in k_H/k_{Br} over the temperature interval from 273 to 313 K results in an error in the differential entropy of activation at 273 K of 0.8 cal/K mol.

Relative rate constants and differential activation parameters for the reactions of aryl radicals with DMF and bromomethanes. The relative rates of reactions (10) and (11) were determined by the

$$Ar^{\cdot} + S\text{-}H(DMF) \xrightarrow{k_H} Ar\text{-}H + S^{\cdot} \quad (10)$$

$$Ar^{\cdot} + CH_mBr_n \xrightarrow{k_{Br}} Ar\text{-}Br + \dot{C}H_mBr_{n-1} \quad (11)$$

procedure outlined above and k_H/k_{Br} were calculated using eqn. (5). The differential activation energies, ΔE_a, corresponding to the differences in E_a between reactions (10) and (11), were obtained from eqn. (12) while the differential entropies of activation at 273 K were calculated using eqn. (8).

$$\ln k_H/k_{Br} = -(\Delta E_a/R)/T + \ln A_H/A_{Br} \quad (12)$$

Rate constant data for 4-nitrophenyl and α-naphthyl radicals are summarized in Tables 1 and 2, respectively. The corresponding differential activation parameters are given in Table 3. A series of reactions between 4-nitrophenyl and $CHBr_3$ were carried out at 0 °C in which n_{DMF}/n_{CHBr_3} varied from about 20 to 80 and k_H/k_{Br} was observed to be within 5 % of the value given in Table 1.

Similar trends in kinetic parameters were observed for the two radicals. In going through the series of reactions of CH_mBr_n at 273 K, the relative k_H/k_{Br} changed from 1.0 to 12.6 to 679 when 4-nitrophenyl was the reactant and from 1.0 to 7.7 to 437 when α-naphthyl was the reactant as m changed from 0 to 1 to 2 (Tables 1 and 2). In both cases ΔE_a, defined as in (12), increased in going from $n=4$ to 3 and then decreased substantially when $n=2$. In both series $\Delta\Delta S^{\neq}_{273}$, defined as in (8) decreased as n decreased.

The extent of reaction (10) relative to that of (11) was observed to be significantly greater for the reactions of 4-nitrophenyl radical than for those of α-naphthyl radical, with relative proportions ranging from 1.4 to 2.3 with the different bromomethanes. When either $CHBr_3$ or CH_2Br_2 was the reactant, the differential activation parameters for the reactions of the two aryl radicals were nearly the same, Table 3. However, the parameters appear to differ

*For each reactant pair, several experiments were necessary to determine the optimum n_{DMF}/n_{BM}. No concentration dependence of k_H/k_{Br} could be detected in any case.

Table 1. Competition kinetic data for the reactions of 4-nitrophenyl radical with bromomethanes.[a]

Bromomethane	n_{DMF}/n_{BM}[b]	t/°C	k_H/k_{Br}[c]
CBr_4	452	0.0	1.56×10^{-3}
CBr_4	452	20.2	1.95×10^{-3}
CBr_4	452	39.3	2.46×10^{-3}
$CHBr_3$	23.8	0.0	1.97×10^{-2}
$CHBr_3$	23.8	20.4	2.60×10^{-2}
$CHBr_3$	23.8	39.8	3.24×10^{-2}
CH_2Br_2	9.51	0.0	1.06
CH_2Br_2	9.51	20.4	1.18
CH_2Br_2	9.51	39.8	1.25

[a] The radical was generated from $ArN_2^+BF_4^-$ (0.0086 mmol) and Bu_4NI (0.01 mmol). [b] The mol ratio of DMF and bromomethane. [c] Calculated from the relative amounts of nitrobenzene and 4-bromonitrobenzene found by GLC analysis as described in the text.

Table 2. Competition kinetic data for the reactions of α-naphthyl radical with bromomethanes.[a]

Bromomethane	n_{DMF}/n_{BM}	t/°C	k_H/k_{Br}
CBr_4	452	0.0	1.11×10^{-3}
CBr_4	452	21.1	1.32×10^{-3}
CBr_4	452	39.4	1.51×10^{-3}
$CHBr_3$	23.8	0.0	8.51×10^{-3}
$CHBr_3$	23.8	20.9	11.4×10^{-3}
$CHBr_3$	23.8	39.5	13.5×10^{-3}
CH_2Br_2	9.51	0.0	0.485
CH_2Br_2	9.51	20.9	0.530
CH_2Br_2	9.51	39.4	0.595

[a] For conditions see Table 1.

Table 3. Differential activation parameters for the reactions of aryl radicals with bromomethanes and DMF.[a]

Bromomethane	ΔE_a[b]	$\Delta\Delta S^{\neq}$[c]
4-Nitrophenyl radical		
CBr_4	2.0	−6
$CHBr_3$	2.1	0
CH_2Br_2	0.7	3
α-Naphthyl radical		
CBr_4	1.3	−9
$CHBr_3$	2.0	−2
CH_2Br_2	0.9	2

[a] Differential activation parameters obtained by correlation of the rate constant data in Tables 1 and 2. [b] The difference in activation energy for H abstraction from DMF and Br abstraction from the bromomethane in kcal/mol. [c] The difference in entropy of activation for the H abstraction from DMF and Br abstraction from the bromomethane at 273 K in units of cal/K mol.

for reactions of the two radicals with CBr_4 but the difference is not large.

Conclusions. The most unexpected feature of the data is that both 4-nitrophenyl and α-naphthyl radicals react with CBr_4 about an order of magnitude more rapidly than with $CHBr_3$ but in both cases the apparent activation energy appears to be lower for the reactions with $CHBr_3$. Thus, if the reactions of the aryl radicals with CBr_4 are to be considered as diffusion controlled as expected from earlier work,[4] the corresponding reactions with $CHBr_3$ must be as well. The order of magnitude difference in rate constants for the reactions of either radical with CBr_4 and $CHBr_3$ is a consequence of the more negative entropies of activation for the reactions with $CHBr_3$. There does not appear to be any reason to believe that the entropies of activation for the reactions of the radicals with CBr_4 should be zero and it is conceivable that these quantities are also negative.

It has recently been pointed out that activation energies calculated for diffusion-controlled second order bimolecular reactions using eqn. (13) and assuming $\Delta S^{\neq}$ equal to zero results in E_a very much

$$E_a = -RT(\ln k_{diff} - \ln ek/h - \ln T) - T\Delta S^{\neq} \qquad (13)$$

greater than the activation energy of diffusion for typical organic molecules.[23] For example, application of (13) assuming k_{diff} equal to 10^{10} M^{-1} s^{-1} and $\Delta S^{\neq}$ equal to zero results in E_a equal to 4.4 kcal/mol which is of the order of twice the value for the activation energies of diffusion for aromatic compounds in DMF. The activation energies for the diffusion of several aromatic compounds in aprotic solvents have recently been determined and those in DMF were found to be equal to 2.4 ± 0.2 kcal/mol.[24] Thus, diffusion-controlled reactions of aromatic compounds in DMF with rate constants in the usual range,[21] from 10^9 to 10^{10} M^{-1} s^{-1}, are predicted by eqn. (13) to have $\Delta S^{\neq}_{298}$ of the order of -7 to -11 cal/K mol. Thus, if the equations, such as (13), based on transition state theory apply to diffusion-controlled reactions entropy effects are of great importance in determining the rate constants.

Orientational constraints and rotational diffusion[25,26] are factors which would be expected to show their influence in the entropy of activation. The bromomethanes should represent a case for which the spherical model with varying degrees of target surface, depending upon the number of Br in the molecule, would be expected to apply. However, the effect of the entropy of activation differences, 6 to 7 cal/K mol, on the relative rates of the reactions of the radicals with CBr_4 and $CHBr_3$ correspond to relative values ranging from 21 to 34 which suggests that differences in target surface on the two bromomethanes can only account for a fraction of the differences in activation entropies.

We find it somewhat surprising that the extent of reaction (10) relative to (11) is greater for 4-nitrophenyl than for α-naphthyl radical. The strongly electron withdrawing nitro group would be expected to significantly reduce the electron density in the ring which in turn should make the 4-nitrophenyl radical relatively electrophilic. Attack on the electron-rich halogen atoms as compared to attack on a hydrogen atom should be more favorable the more electrophilic the radical. A related series of experiments has shown this to be the case when different 4-substituted nitrophenyl radical reactions are compared.[27] The comparison between 4-nitrophenyl and α-naphthyl may involve factors other than relative nucleophilicity since the structures differ considerably. The effect of electron withdrawing groups on the nucleophilicity of radicals has been discussed in terms of frontier molecular orbital theory.[28]

EXPERIMENTAL

Reagent grade DMF was passed through a column of neutral alumina before use. The diazonium fluoroborates were prepared by a standard procedure[29] and stored at −5 °C. The bromomethanes were reagent grade and used without further purification.

GLC analyses were carried out using a 5 % OV-17 column in a Perkin Elmer 3920B gas chromatograph equipped with a Hewlett Packard 3380S integrator. The analysis procedure was described in an earlier section.

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