η^3-allylic complexes then corresponds to a conversion of the metalla fragment into a formal analogue to an sp^3-CH group. Hoffmann has calculated that such an $Mn(CO)_4$ group should have a slight square-pyramidal distortion,[7] where the two axial CO ligands are tilted *away* from the η^3-allyl ligand. In complex **14**, the two axial CO ligands are tilted away from the η^3-allyl ligand [the C(1)–Mn–C(4) angle is 168.3 (6)°]. If this distortion is caused by primarily electronic factors, then the formal description of these η^3-allyl complexes, like **5** as 1-metallabicyclo[1.1.0]butanes becomes more accurate.[33]

Acknowledgment. C.M.L. thanks the National Science Foundation (Grant No. CHE-8106140), the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the University Research Council of Vanderbilt University for support of this research. C.M.L. also acknowledges support from the Alfred P. Sloan Foundation as a Research Fellow. P.G.L. acknowledges support from NIH BRSG (Grant No. RR 07089-13).

Registry No. 6, 73426-85-4; **7**, 73426-87-6; **8**, 87842-20-4; **9**, 67619-57-2; **10**, 69090-82-0; **11**, 87842-22-6; **12**, 87842-24-8; **13**, 87842-26-0; **14**, 87842-27-1; **15**, 87842-29-3; **16**, 87842-31-7; **18**, 87861-46-9; **21**, 87869-34-9; i-PrC(O)$Mn(CO)_5$, 15022-36-3; BF_3, 7637-07-2.

Supplementary Material Available: A complete listing of final positional and thermal parameters (including hydrogen atoms), final observed and calculated structure factors, selected bond distances and angles (including a labeled ORTEP diagram) of the anion of **14** having a 29% occupation factor, a labeled ORTEP diagram of the PPN cation, and selected least-squares planes data for **14** (30 pages). Ordering information is given on any current masthead page.

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(33) We do not wish to imply that our results prove that a pericyclic mechanism is correct. In ref 2, we also presented a mechanism involving electrophilic attack by a positively charged acyl carbon atom on the π-electron pair of an adjacent metal–carbon multiple bond with a concomitant reduction of the metal atom. A referee has suggested the inclusion of a "simple vinyl migration to the carbene in order to form the allyl." This mechanism is essentially the same as our **4** to **5** conversion where the electron pairs are moved in a reversed direction.

The E2 Transition State: Elimination Reactions of 2-(2,4-Dinitrophenyl)ethyl Halides

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Abstract: The base-catalyzed elimination reactions of 2-(2,4-dinitrophenyl)ethyl halides in aqueous solution have been investigated. The relative rate constants for the hydroxide ion catalyzed reactions of the fluoride, chloride, bromide, and iodide are 1:2:9:14, respectively, and there is no hydrogen–deuterium exchange into either the fluoride or chloride substrates when the reactions are run in deuterium oxide with deuteroxide ion as the base catalyst. The reactions are general-base catalyzed with Brønsted β values increasing from 0.42 for the iodide to 0.54 for the fluoride, but decreasing as the β-phenyl substituent is made more electron withdrawing in the series 2-(p-nitrophenyl)ethyl bromide (0.61) and 2-(2,4-dinitrophenyl)ethyl bromide (0.46). These results are consistent with an E2 mechanism for these substrates and a reaction coordinate that has a major proton transfer component, as described on More O'Ferrall–Jencks energy surfaces. The decrease in β values as the β-phenyl substituent is made more electron withdrawing reverses previously reported trends of increasing β values in the series 2-phenylethyl bromide (0.51) and 2-(p-nitrophenyl)ethyl bromide (0.61). This inversion in the trend of β values means that substrate selectivity undergoes an inversion with increasing substrate reactivity; it is consistent with a clockwise rotation of the E2 reaction coordinate, from one with a major diagonal component for 2-phenylethyl halides to one with a major proton transfer component for the nitro-activated derivatives.

2-Arylethyl derivatives have played a central role in studies of olefin-forming β-elimination reactions and in understanding the relationship between the structure of the E2 transition state and changes in reactant and catalyst structure and reaction conditions.[1,2] Results from these studies indicate that as the β-phenyl substituent is made more electron withdrawing the extent of proton transfer to the base catalyst increases for substrates with good leaving groups, such as halide ions,[3,4] but decreases for substrates with poorer leaving groups, such as ammonium ions.[1,2,5-7] Based on these and many other results, including Hammett ρ values which are larger for ammonium ion than halide ion substrates,[1,2] a mapping out of the E2 transition state for these reactions on More O'Ferrall–Jencks energy surfaces[8,9] has been made. For 2-arylethyl halides the results are consistent with a "central" transition state and a reaction coordinate with a large diagonal component.[5,7] For (2-arylethyl)ammonium ions, however, a transition state is suggested with more carbanion character and a reaction coordinate that has a major component of proton transfer.[5,7,10] If this change in behavior is a result of a shift to the E1cB borderline for the ammonium ion substrates,[5,7] then a similar change in behavior should be observed for a series of

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Table I. Rate Constants and Brønsted β Values for the Base-Catalyzed Elimination Reactions of 2-(*p*-Nitrophenyl)ethyl Bromide and 2-(2,4-Dinitrophenyl)ethyl Halides[a]

substrate	10^2k, M^{-1} s^{-1}				
	HO^-	$CF_3CH_2O^-$ [b]	$(CF_3)_2CHO^-$ [c]	$CH_3CH_2O^-$ [d]	β[e]
$2,4\text{-}(NO_2)_2C_6H_3CH_2CH_2F$	2.07	1.09	0.0621	753	0.54
$2,4\text{-}(NO_2)_2C_6H_3CH_2CH_2Cl$	4.23	2.21	0.125	2090	0.54
$2,4\text{-}(NO_2)_2C_6H_3CH_2CH_2Br$	18.2	10.5	0.700	7800	0.46
$2,4\text{-}(NO_2)_2C_6H_3CH_2CH_2I$	28.5	15.8	1.41	16700	0.42
$4\text{-}NO_2C_6H_4CH_2CH_2Br$	0.269[f]	0.0891	0.00348	47.8	0.61[g]

[a] In aqueous solution at 25 °C and $I = 1.0$ M maintained with potassium chloride. [b] In buffer solutions of fraction free base = 0.50. [c] In buffer solutions of fraction free base = 0.50. [d] In ethanol at 25 °C; $[NaOEt] = (3.09 \times 10^{-4})-(9.5 \times 10^{-2})$ M. [e] Calculated from plots of log *k*, using HO^-, $CF_3CH_2O^-$, and $(CF_3)_2CHO^-$ as base catalysts, against log *k* for 2-(*p*-nitrophenyl)ethyl bromide for which we take $\beta = 0.61$.[35] [f] $k = 0.282 \times 10^{-2}$ M^{-1} s^{-1} from ref 11 and 0.263×10^{-2} from ref 18. [g] Reference 35.

2-arylethyl halides if the E2 transition state for these substrates were also shifted to the E1cB borderline by strongly activating β-phenyl substituents.

We were also interested in learning if a change to the E1cB mechanism would be observed for substrates with weakly basic halide ion leaving groups and strongly activating β-phenyl substituents. Although an E1cB mechanism has been reported recently for (2-(*p*-nitrophenyl)ethyl)ammonium ions, 2-(*p*-nitrophenyl)ethyl halides still react by the E2 mechanism.[11] An E2 mechanism has also been reported in methanol for 1-fluoro-2,2-bis(4-nitrophenyl)ethane.[12] We therefore undertook a study of the elimination reactions of 2-(2,4-dinitrophenyl)ethyl halides in aqueous solution. These substrates represent the most strongly activated ones studied so far in the 2-arylethyl series.

$$2,4\text{-}(NO_2)_2C_6H_3CH_2CH_2X$$
$$X = F, Cl, Br, I$$

Experimental Section

All melting points were measured on a Thomas Hoover Melting Point Apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Varian EM 360 spectrometer. Kinetic experiments were conducted on a Cary Model 17D or Pye Unicam Model SP1750 spectrophotometer; UV–vis spectra were recorded on the Cary Model 17D.

Materials. Inorganic salts were reagent grade and used without further purification. All other reagents were either distilled or recrystallized prior to use. 2-(*p*-Nitrophenyl)ethyl bromide was purchased from Aldrich. Absolute ethanol was dried over magnesium turnings and then distilled. Solutions of sodium ethoxide were prepared by adding sodium metal to ethanol and standardized by titration against potassium hydrogen phthalate.

2-(2,4-Dinitrophenyl)ethyl Fluoride. 2-(*p*-Nitrophenyl)ethyl fluoride was first prepared from 2-phenylethyl alcohol as reported by Winey and Thornton[7] and then nitrated[13] to yield a pale-yellow oil which crystallized upon cooling in a dry-ice–acetone bath. The resulting white solid was recrystallized from 95% ethanol: mp 29.5–30.5 °C; ^{1}H NMR ($CDCl_3$) δ 3.20, 3.65, 4.39, 5.16 (dt, 4 H, J = 46, 26, 6 Hz), 7.66 (d, 1 H), 8.38, 8.48 (dd, 1 H, J = 12, 3 Hz), 8.84 (d, 1 H).

2-(2,4-Dinitrophenyl)ethyl Chloride. 2-Phenylethyl chloride, prepared from 2-phenylethyl alcohol and thionyl chloride,[14] was nitrated, and 2-(*p*-nitrophenyl)ethyl chloride was obtained upon cooling the reaction mixture. Subsequent nitration of 2-(*p*-nitrophenyl)ethyl chloride resulted in a pale-yellow oil which was recrystallized from 95% ethanol: mp 25.5–26.0 °C; ^{1}H NMR ($CDCl_3$) δ 3.50 (t, 2 H), 3.90 (t, 2 H), 7.70 (d, 1 H), 8.38, 8.52 (dd, 1 H, J = 12, 3 Hz), 8.88 (d, 1 H).

2-(2,4-Dinitrophenyl)ethyl Bromide. This compound was prepared by nitration of 2-(*p*-nitrophenyl)ethyl bromide and was recrystallized from 95% ethanol: mp 37.5–38.0 °C; ^{1}H NMR ($CDCl_3$) δ 3.69 (m, 4 H), 7.70 (d, 1 H), 8.40, 8.54 (dd, 1 H, J = 12, 3 Hz), 8.90 (d, 1 H).

2,4-Dinitrostyrene. To a 150-mL solution of 2-(2,4-dinitrophenyl)ethyl chloride in 95% ethanol was added 6.5 mL of 1.0 M potassium hydroxide (6.5 mmol). The solution turned a blue-violet and then faded to a brownish-yellow. After 1 h a grey precipitate was filtered and washed with both ethanol and acetone. The resulting white solid did not melt below 230 °C and was insoluble in common solvents. This compound fits the description of the compound suggested by Wiley and Behr[15] to be 2,4-dinitrostyrene. However, when the filtrate was poured into ice water a pale-yellow precipitate was collected after 5 h. This material was recrystallized from 95% ethanol: mp 55.5–56.5 °C; UV_{max} (H_2O) 275 nm (ϵ 11 960); ^{1}H NMR (acetone-d_6) δ 5.78 (d, 1 H), 6.16 (d, 1 H, J = 18 Hz), 7.23 (dd, 1 H), 8.12 (d, 1 H), 8.50, 8.63 (dd, 1 H), 8.92 (d, 1 H).

Kinetics. Kinetic experiments were carried out by following spectrophotometrically the appearance of 2,4-dinitrostyrene at 290 nm. Reactions were carried out at 25 °C in aqueous solution with a large excess of buffer at ionic strength 1.0 M maintained with potassium chloride. Cuvettes were temperature equilibrated for at least 20 min prior to a kinetic run. Reactions of 2-(2,4-dinitrophenyl)ethyl halides were followed to completion and plots of log ($A_\infty - A$) against time obeyed good pseudo-first-order kinetics. The slower reactions of 2-(*p*-nitrophenyl)ethyl bromide in trifluoroethanol and hexafluoro-2-propanol buffer solutions were followed by the method of initial rates at 334 nm with $k_{obsd} = \Delta A/[S]_0(\epsilon_p - \epsilon_a)\Delta t$ in which ϵ_a and ϵ_p are the extinction coefficients of 2-(*p*-nitrophenyl)ethyl bromide (778) and *p*-nitrostyrene (8818), respectively, and $[S]_0$ is the initial substrate concentration.

Measurements of pH were made on a Beckman Altrex 71 pH Meter with a Beckman 39505 combination electrode. The pH of buffer solutions of hexafluoro-2-propanol increased about 0.14 units with increasing buffer concentration (0.06–0.30 M base). For these reactions, however, no correction to k_{obsd} is required because there is no contribution from the hydroxide ion reaction at these pH values. Buffer solutions of trifluoroethanol were prepared by diluting a 1.0 M stock buffer solution (fraction free base = 0.5) with a solution at the same pH and ionic strength but without buffer.

Hydrogen–Deuterium Exchange Experiments. In a typical experiment 0.1 g of substrate (both the fluoride and chloride substrates were studied) was first dissolved in 0.2 mL of acetonitrile and then added to 5.0 mL of 0.093 M potassium deuteroxide ion in deuterium oxide. The reaction was quenched with 1.0 M HCl at 20, 50, and 80% reaction. The substrate and product were then extracted into CH_2Cl_2, and the ^{1}H NMR spectrum was recorded.

Product Analysis. The product of the base-catalyzed reactions of 2-(2,4-dinitrophenyl)ethyl halides was shown to be 2,4-dinitrostyrene by comparing the UV–vis spectrum of the product of each reaction with the UV–vis spectrum of an authentic sample of 2,4-dinitrostyrene. For 2-(2,4-dinitrophenyl)ethyl iodide the UV spectrum of iodide ion was first subtracted from the observed spectrum. In basic solution 2,4-dinitrostyrene decomposes slowly under the reaction conditions, but this decomposition is much slower than the elimination reactions.

Results

The elimination reactions of 2-(2,4-dinitrophenyl)ethyl halides follow the rate law of eq 1 in aqueous solution at 25 °C and ionic strength 1.0 M maintained with potassium chloride. The rate constants for the hydroxide ion and buffer catalyzed reactions are k_{OH} and k_B, respectively. Rate constants for catalysis by hydroxide ion were obtained in dilute solutions of potassium hydroxide in water. Rate constants for the buffer-catalyzed reactions were obtained from the slopes of plots of k_{obsd} against buffer base concentration at constant pH and generally at five or more buffer concentrations. Rate constants for catalysis by ethoxide ion were obtained in dilute solutions of sodium ethoxide in ethanol. Plots of k_{obsd} against ethoxide ion concentration were linear up to ca.

$$k_{obsd} = k_{OH}[OH^-] + k_B[B^-] \qquad (1)$$

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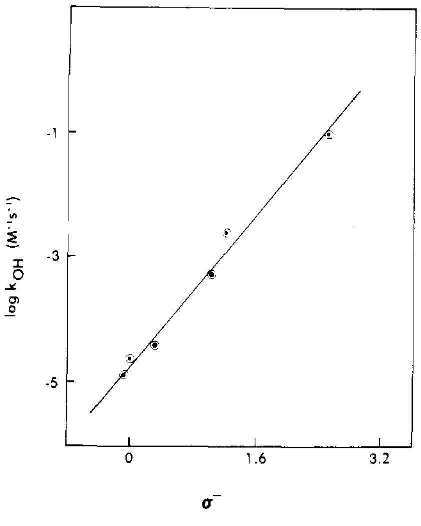


Figure 1. Hammett plot for the elimination reactions of 2-arylethyl bromides catalyzed by hydroxide ion. Rate constants for the unsubstituted, *p*-methoxy, *m*-chloro, and *p*-cyano derivatives are taken from ref 18.

0.02 M base concentration, but showed downward curvature at higher concentrations of ethoxide ion. The rate constants were always calculated from the linear portion of these plots at low ethoxide ion concentrations. Table I summarizes the second-order rate constants for the substrates investigated in this study.

There was no detectable incorporation of deuterium, as determined by ^1H NMR, when the reactions of the fluoride and chloride substrates were conducted in deuterium oxide with deuteroxide ion as the base catalyst.

A Hammett plot using σ^- substituent constants[16] for the hydroxide ion catalyzed reactions of 2-arylethyl bromides is shown in Figure 1. A σ^- value of 1.24 was taken for the *o*-nitro group based on the ionization constants of ortho-substituted phenols.[17] Data for the *p*-methoxy, *m*-chloro, *p*-cyano, and unsubstituted compounds were taken from the work of Yano et al.[18] The rate constant of $2.69 \times 10^{-3}\ M^{-1}/s^{-1}$ for 2-(*p*-nitrophenyl)ethyl bromide agrees well with the value of $2.82 \times 10^{-3}\ M^{-1}/s^{-1}$ reported by Keeffe and Jencks[11] and $2.63 \times 10^{-3}\ M^{-1}/s^{-1}$ reported by Yano et al.[18]

Figure 2 shows that the reaction of 2-(2,4-dinitrophenyl)ethyl fluoride is general-base catalyzed: the observed rate constant increases linearly with increasing concentrations of trifluoroethoxide ion in buffer solutions at constant pH; catalysis is also observed in hexafluoro-2-propanol buffer solutions. A similar increase in rate constant as a function of buffer base concentration is observed for the other 2-(2,4-dinitrophenyl)ethyl halides (plots not shown).

Apparent Brønsted β values were calculated from plots of log k for the 2-(2,4-dinitrophenyl)ethyl halides, using hydroxide ion and the anions of trifluoroethanol and hexafluoro-2-propanol as base catalysts, against log k for 2-(p-nitrophenyl)ethyl bromide for which we take $\beta = 0.61$. A β value of 0.61 is the average of β values of 0.55 and 0.67 which have been previously reported for this substrate in 60 vol% dimethyl sulfoxide in water with oxyanions[3] and in ethanol with phenoxide ions,[4] respectively. The Brønsted β values calculated in this way increase from 0.42 for the iodide to 0.54 for the fluoride (Table I).

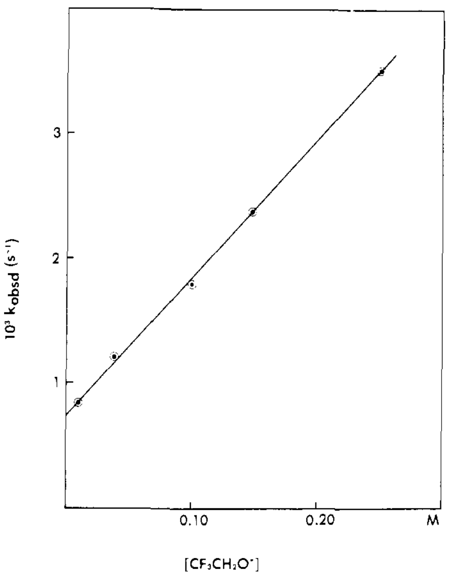
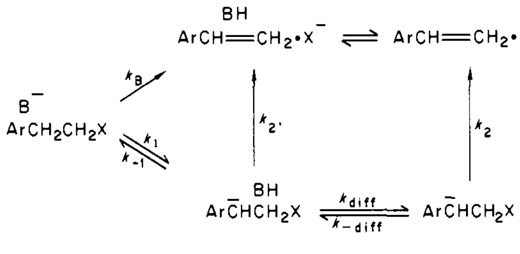


Figure 2. Dependence of k_{obsd} on trifluoroethoxide ion concentration for the reaction of 2-(2,4-dinitrophenyl)ethyl fluoride at 25 °C, $I = 1.0$ M. Fraction of free base = 0.5, pH 12.41.

Scheme I



Discussion

The observed general-base catalysis with Brønsted β values ranging from 0.42 to 0.54 (Table I) and the lack of hydrogen–deuterium exchange when the elimination reactions of the fluoride and chloride substrates were conducted in deuterium oxide rule out both the $(\mathrm{ElcB})_{\mathrm{rev}}$ mechanism, for which specific base catalysis and hydrogen–deuterium exchange are required, and the $(\mathrm{ElcB})_{\mathrm{ip}}$ mechanism, for which a β value near 1 is expected—the proton is fully transferred to the base in the transition state. An ion-pair mechanism is a preassociation mechanism in reverse.[19] A β value of ca. 1 is also expected for a mechanism in which diffusion of the catalyst is rate limiting (k_{diff}, Scheme I).

Koch and co-workers[20] have demonstrated an internal return mechanism for the elimination reactions of some halogenated 2-phenylethyl derivatives in ethanol and methanol. An internal return mechanism, in which formation (k_1) and breakdown ($k_{2'}$) of an ion-pair intermediate are both partially rate limiting, provides a possible alternative to the concerted E2 mechanism[20] (Scheme I). An internal return mechanism for the reactions of 2-(2,4-dinitrophenyl)ethyl halides in aqueous solution, however, can be ruled out. An ion-pair or encounter complex formed from 2-(2,4-dinitrophenyl)ethyl halides is expected to have a relatively long lifetime with respect to proton transfer. For example, in water the rate of protonation of 2,6-dinitrobenzyl anion by water and the hydronium ion is relatively slow: 9 s^{-1} and $10^5\ M^{-1}\ s^{-1}$, respectively.[21] This means that the conjugate acid of the catalyst should have time to diffuse away from the initially formed ion pair (k_{diff}) faster than this intermediate is reprotonated (k_{-1}). Under this condition, an internal return mechanism is not possible: if k_2 is greater than k_{-diff} the mechanism will be $(\mathrm{ElcB})_{\mathrm{irr}}$, whereas if k_2 is less than k_{-diff} the substrate will be equilibrium with the free carbanion and some hydrogen–deuterium exchange into the substrate ought to be observed—it is also possible that k_2' will

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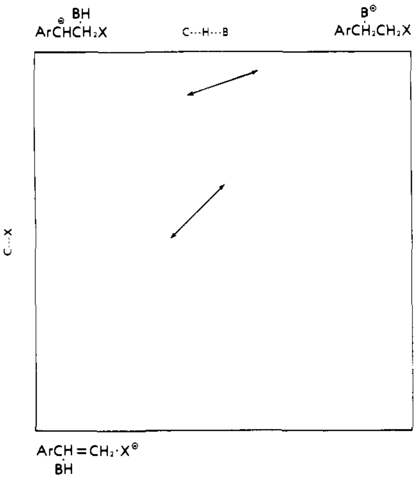

Figure 3. More O'Ferrall–Jencks energy surface for the β-elimination reactions of 2-arylethyl halides. Proton transfer occurs along the x axis and leaving group bond cleavage along the y axis. A reaction coordinate with a major component of proton transfer is drawn near the ElcB borderline, consistent with the structure–reactivity behavior of the p-nitrophenyl and (2,4-dinitrophenyl)ethyl halides. Also included, near the center of the diagram, is a reaction coordinate with a major diagonal component consistent with the data for the less activated 2-arylethyl halides.

be greater than k_{diff}, but this would make k_1 rate limiting, $(\text{ElcB})_{\text{irr}}$.

Table I shows that the relative rate constants for the hydroxide ion catalyzed reactions of the fluoride, chloride, bromide, and iodide substrates are in the order 1:2:9:14. This result indicates significant cleavage or weakening of the carbon–halogen bond in the transition state and suggests an E2 mechanism.[22] For the ethoxide ion catalyzed reactions in ethanol the relative rate constants are 1:3:10:22 (Table I). This effect is similar to the leaving group effect observed in water and is consistent with an E2 mechanism in ethanol also. The opposite order of halogen mobility is expected for the $(\text{ElcB})_{\text{irr}}$ mechanism where the carbon–halogen bond is intact in the transition state, and the leaving group should affect the rate only through its polar effect.[22]

Alhberg and Thibblin have recently questioned this criterion of mechanism (the element effect) and have suggested that hyperconjugation in the proton-transfer step of an $(\text{ElcB})_{\text{irr}}$ mechanism is important and increases in the order fluorine, chlorine, bromine, and iodine and that many reactions previously thought to follow the E2 mechanism may instead follow the stepwise ElcB mechanism.[23-25] Although it is difficult to distinguish an E2 mechanism from an $(\text{ElcB})_{\text{irr}}$ mechanism in which there is orbital interaction between the carbanionic charge and the carbon leaving group bond, the absence of a primary chlorine leaving group isotope effect in the elimination reaction of 1,1-bis(p-nitrophenyl)-1,1-dichloroethane,[26] a substrate believed to follow the $(\text{ElcB})_{\text{irr}}$ mechanism,[26] means that hyperconjugation is not important in this system.[3,11] Furthermore, in the elimination reactions of 2-(phenylsulfonyl)ethyl halides[27] and 9-halogeno-9,9′-bifluorenyls[28] the fluoride substrates are more reactive than the chlorides, the order expected for a classical $(\text{ElcB})_{\text{irr}}$ mechanism for the fluorides. If hyperconjugation is significant in elimination reactions, then substrates that react by the $(\text{ElcB})_{\text{irr}}$ mechanism (independently established) should be found which show heavy-atom leaving group, α-carbon, and α-hydrogen isotope effects.

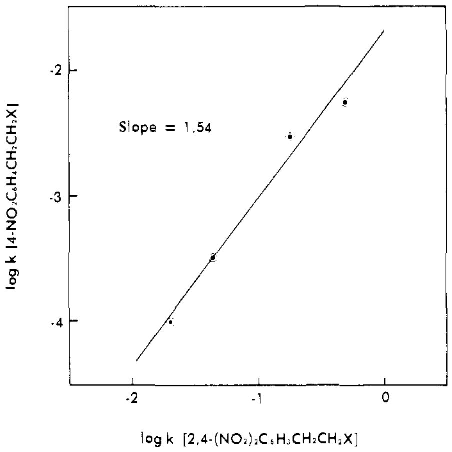

Figure 4. Plot of log k for the hydroxide ion catalyzed reactions of 2-(p-nitrophenyl)ethyl halides against log k for 2-(2,4-dinitrophenyl)ethyl halides at 25 °C, and I = 1.0 M (KCl). The halogens included in this plot are the fluoride, chloride, bromide, and iodide.

Changes in structure–reactivity parameters that reflect changes in the structure of the E2 transition state, as reactant and catalyst structure and reaction conditions are changed, can provide additional evidence for an E2 mechanism in elimination reactions. These changes can be usefully described on energy surfaces of the More O'Ferrall–Jencks type.[8,9] An energy surface for the elimination reactions of the 2-(2,4-dinitrophenyl)ethyl halides is shown in Figure 3. The base and the substrate are located in the upper right hand corner of the diagram; proton transfer occurs along the x axis and bond cleavage along the y axis. The results will be discussed now in the context of these energy surfaces.

Figure 4 shows that the rate constant for elimination is less sensitive to changes in the leaving halogen for 2-(2,4-dinitrophenyl)ethyl halides than for the less reactive 2-(p-nitrophenyl)ethyl halides.[11] The plot of log k for the p-nitro compounds against log k for the dinitro compounds is linear with a slope of 1.54 (Figure 4). Similarly, a plot of log k for the ethoxide ion catalyzed reactions in ethanol of 2-phenylethyl halides,[29] substrates which are generally agreed to react by the E2 mechanism,[20a,30] against log k for the reactions in ethanol of 2-(2,4-dinitrophenyl)ethyl halides is also linear but with a slope of 3.29 (plot not shown). In neither case is there a deviation of either the chloride or fluoride substrates from these plots that would indicate a change to an ElcB mechanism within these series. On the other hand, the greater reactivity of the fluoride than chloride substrates in the reactions of 2-(phenylsulfonyl)ethyl halides,[27] 9-halogeno-9,9′-bifluorenyls,[28] and *trans*-1,2-dihalogenoacenaphthenes[31] means that the fluoride substrates would show positive deviations from such plots.[32] This is consistent with change to an $(\text{ElcB})_{\text{irr}}$ mechanism for the fluorides in these systems.[27,28,31]

This decrease in the element effect as the β-phenyl substituent is made more electron withdrawing is consistent with a variable-E2 transition-state structure and a movement toward the top of the surface in Figure 3 that results from lowering the energy of the carbanion intermediate in the upper left hand corner of the diagram. This effect corresponds to a negative $p_{yy'}$ interaction coefficient that describes the interaction between the leaving group and the β-phenyl substituent in these systems.[34]

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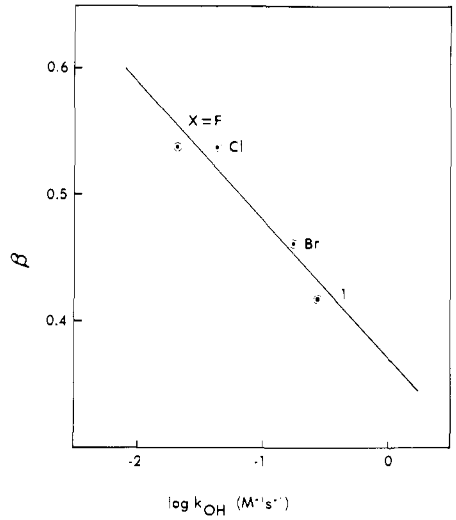

Figure 5. Dependence of Brønsted β values on log k for the hydroxide ion catalyzed reactions of 2-(2,4-dinitrophenyl)ethyl halides at 25 °C, I = 1.0 M (KCl).

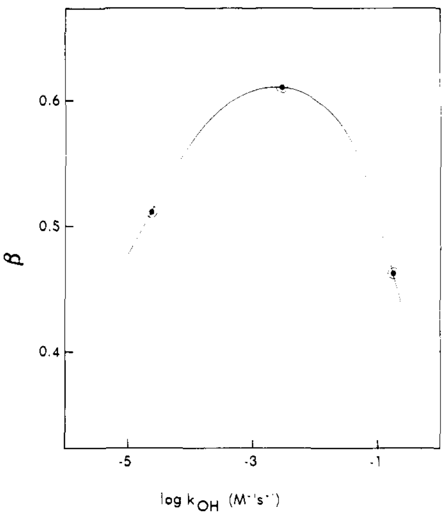

Figure 6. Dependence of Brønsted β values on log k for the hydroxide ion catalyzed reactions of 2-phenylethyl bromide,[18,35] 2-(p-nitrophenyl)ethyl bromide,[35] and 2-(2,4-dinitrophenyl)ethyl bromide.

Figure 5 shows that the Brønsted β values increase from 0.42 to 0.54 as the leaving halogen is changed from iodine to fluorine. This corresponds to greater proton transfer to the base catalyst as the leaving group becomes less nucleofugal and a shift to the left on the energy surface. This effect corresponds to a positive p_{xy} interaction coefficient that describes the interaction between the base catalyst and the leaving group[34] and provides additional evidence for the E2 mechanism.

The p_{xy} coefficient has recently been suggested as a means of making the ordinarily difficult distinction between the E2 and the (ElcB)$_{irr}$ mechanisms.[3] Whereas proton transfer is expected to increase as the leaving group is made less nucleofugal for the E2 mechanism, a decrease or no dependence of β on the leaving group is expected for the (ElcB)$_{irr}$ mechanism. This different behavior corresponds to a difference in the orientation of the reaction coordinates for these two different mechanisms. A change from a positive p_{xy} coefficient for substituted (2-arylethyl)quinuclidinium ions, which react by an E2 mechanism, to a zero p_{xy} coefficient for the p-nitrophenyl derivatives, which react by the (E1B)$_{irr}$ mechanism, provides support for this criterion of mechanism.[3]

The Brønsted β value is smaller for 2-(2,4-dinitrophenyl)ethyl bromide (0.46) than 2-(p-nitrophenyl)ethyl bromide (0.61) (Table I). This indicates that proton transfer decreases as the β-phenyl substituent is made more electron withdrawing in this series; it corresponds to a shift to the right on the energy surface that results from lowering the energy of the carbanion intermediate. This corresponds in turn to a negative $p_{xy'}$ coefficient that describes the interaction between the base catalyst and the β-phenyl substituent.[34]

Structure–reactivity parameters, and changes in these parameters for a given system, allow for a mapping out of transition-state structure on these energy surfaces.[5,7,8,34] For example, a more-electron-withdrawing β-phenyl substituent increases the degree of proton transfer in the reactions of 2-arylethyl bromides, as shown by the increase in β values from 0.51 for 2-phenylethyl bromide to 0.61 for 2-(p-nitrophenyl)ethyl bromide.[3,4,35] In the E2 reactions of (2-arylethyl)ammonium ions, however, proton transfer decreases, as shown by the increase in the β hydrogen isotope effect from 2.6 to 4.2 in the reactions of (2-arylethyl)trimethylammonium ions[5,6] and the small decrease in β values from 0.93 to 0.87 in the reactions of (2-arylethyl)quinuclidinium ions.[3] These and other data have led to the hypothesis that substrates with good leaving groups, such as the halide ions, react through "central" transition states with reaction coordinates that have a large diagonal component, whereas substrates with poorer leaving groups, such as ammonium ions, react through transition states with greater carbanion character and reaction coordinates that have a large component of proton transfer.[5,7,10] It has been suggested, however, that changes in the β hydrogen isotope effect in the reactions of (2-arylethyl)ammonium ions may not represent real changes in the degree of proton transfer in the transition state. Instead, these changes may represent changes in the degree of proton tunneling[36] and changing contributions of heavy-atom motion to motion along the reaction coordinate.[6] This casts a shadow over conclusions based on these isotope effects; other probes of proton transfer, such as solvent isotope effects (k_{OD}/k_{OH}) and Brønsted β values, may be helpful in this regard.

The "normal" element effect along with the negative $p_{xy'}$, $p_{yy'}$, and positive p_{xy} coefficients are consistent with a concerted E2 mechanism for these compounds, and a reaction coordinate that has a large component of proton transfer (Figure 3). These results are not consistent with a "central" transition state, and a reaction coordinate that has a large diagonal component for which an increase, not a decrease, in proton transfer is predicted as the β-phenyl substituent is made more electron withdrawing.[5,7,8,34,37,38]

All the results taken together for the 2-arylethyl halides show that as the β-phenyl substituent is made more electron withdrawing there is first an increase in Brønsted β values, that has been previously reported,[3,4] and then a decrease: 2-phenylethyl (0.51),[35] 2-(p-nitrophenyl)ethyl (0.61), and 2-(2,4-dinitrophenyl)ethyl bromides (0.46). This represents an inversion in the trend of β with increasing substrate reactivity that can be explained by a change in the structure of the E2 transition state and a clockwise rotation of the reaction coordinate relative to the proton-transfer axis: from one with a major diagonal component for the unactivated 2-phenylethyl halides to one with a large proton transfer component for the nitro-activated compounds (Figure 3).

These β values are plotted against log k for the hydroxide ion catalyzed reactions in water in Figure 6. This figure illustrates an extraordinary reactivity–selectivity relationship; it shows that selectivity undergoes an *inversion* with increasing substrate reactivity. It is unlikely that this inversion is a result of a steric effect of the ortho nitro group, because the rate constant for the hydroxide ion catalyzed reaction of 2-(2,4-dinitrophenyl)ethyl

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[35] A β value of 0.61 for 2-(p-nitrophenyl)ethyl bromide and 0.51 for 2-phenylethyl bromide are the averages of β values of 0.55[3] and 0.67[4] for the nitro compound and 0.48[3] and 0.55[4] for the phenyl compound that have been previously reported for these substrates in 60 vol% Me$_2$SO in water[3] and in ethanol,[4] respectively.

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bromide falls on the Hammett plot with other meta- and para-substituted compounds studied by Yano et al.[18] using a σ^- value of 1.24 for the ortho nitro group that is based on the ionization of ortho-substituted phenols[17] (Figure 1).

This inversion in the trend of β values means that Hammett plots for these reactions, catalyzed by weaker base catalysts than the hydroxide ion, will show positive deviations for 2-(2,4-dinitrophenyl)ethyl bromide. This is because with weaker base catalysts, the decrease in rate constant will be greater for the *p*-nitro compound, which has the largest β value (0.61), than for *both* the less activated and the dinitro bromides which have smaller β values.

Positive deviations from Hammett plots, which characterized a change in mechanism, have been previously observed in the reactions of (2-arylethyl)quinuclidinium ions.[3] The results reported here suggest that positive deviations from Hammett plots are also expected in elimination reactions that do not reflect a change in mechanism, but rather a large change in the orientation of the reaction coordinate, and structure of the E2 transition state that occurs near the ElcB borderline.

Registry No. 2,4-$(NO_2)_2C_6H_3CH_2CH_2F$, 87902-03-2; 2,4-$(NO_2)_2C_6H_3CH_2CH_2Cl$, 63070-32-6; 2,4-$(NO_2)_2C_6H_3CH_2CH_2Br$, 60680-77-5; 2,4-$(NO_2)_2C_6H_3CH_2CH_2I$, 87902-04-3; 4-$NO_2C_6H_4CH_2CH_2Br$, 5339-26-4; 4-$NO_2C_6H_4CH_2CH_2F$, 56153-06-1; 4-$NO_2C_6H_4CH_2CH_2Cl$, 20264-95-3; 2,4-$(NO_2)_2C_6H_3CH{=}CH_2$, 2287-45-8; HO^-, 14280-30-9; $CF_3CH_2O^-$, 24265-37-0; $(CF_3)_2CHO^-$, 44870-01-1; $CH_3CH_2O^-$, 16331-64-9; 2-phenylethyl alcohol, 60-12-8; 2-phenylethyl chloride, 622-24-2.

Relative Rate Constants of Hydrogen Transfer to Benzyl Radical

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Abstract: A method has been developed for measuring relative rate constants for hydrogen transfer from reactive donor compounds to the benzyl radical generated by thermolysis of dibenzylmercury. Relative rate constants were measured against the rate constant for a reference donor, triphenylsilane-*d*, for 23 hydrogen donor compounds at 170 °C. The values range from 0.12 for mesitylene to 37 for 9,10-dihydroanthracene. A correlation was found between the logarithm of the relative rates of hydrogen transfer from arylmethyl donors and estimates of the resonance stabilization energies of the arylmethyl radicals thus formed. The influence of stereoelectronic factors, steric inhibition to resonance, and angle strain on the relative rates is also discussed.

Investigations of the mechanism of direct coal liquefaction have often used benzyl radical as a model of reactive species generated under pyrolytic conditions. The quenching of such radicals by hydrogen transfer from so-called donor solvents is an important step in much of this chemistry.[1] Although some work has been reported concerning rates of hydrogen transfer to resonance-stabilized radicals,[2-7] information regarding patterns of selectivity of benzyl radical, especially toward hydroaromatic donors, is lacking. The present work employs a method based on competitive kinetics to obtain relative rate constants for hydrogen transfer transfer to benzyl radical from 23 compounds all measured against a common reference compound, the deuterium donor triphenylsilane-*d*.

Experimental Section

Materials. (Reference to a brand or company name is made to facilitate understanding and does not imply endorsement by the U.S. Department of Energy.) All hydrogen donors were determined to be greater than 98.5% pure by capillary gas chromatographic analysis unless otherwise noted. Dibenzylmercury (Alfa) was recrystallized three times from ethanol, mp 110.5-111.5 °C (lit. 111 °C). Dihydropyrene was a mixture of 53% dihydropyrene and 47% pyrene, prepared in our laboratory by the reduction of pyrene.[8] The 4,5,6,7-tetrahydrobenzothiophene, 99.5% by capillary gas chromatography, was kindly donated by R. Winans. Triphenylsilane-*Si-d* was synthesized after the method of Gilman and Dunn[9] by lithium aluminum deuteride (Aldrich, 98 atom % D) reduction of triphenylsilyl chloride or triphenylsilyl bromide in refluxing ether. Triphenylsilane-*d*, recrystallized from hexanes (mp 40.0-41.5 °C, uncorrected), was determined to be 98.5% deuterated by proton NMR spectroscopy employing standard addition techniques. Toluene-α-*d* was synthesized via the Grignard reaction with benzyl chloride and magnesium followed by quenching with deuterium oxide. Toluene-α-*d* prepared in this manner had a deuterium content of 96.5% as determined by the method of standard additions using proton NMR spectroscopy.

Kinetic Measurements. Kinetic experiments were performed in microautoclaves made from $^1/_2$ in. by 2 in. stainless steel threaded unions fitted with Swagelok caps. In all cases, both hydrogen and deuterium donors were added to the microautoclave in 10-fold excess (or more) over the yield of toluene, thus assuring that pseudo-first-order kinetics was maintained with regard to both the hydrogen donor and triphenylsilane-*d*. The Swagelok cap was tightened and the contents mixed. The reactors were placed in an air convection oven at 170 ± 2 °C for 18 h. After reaction, the solutions were transferred to Teflon-capped vials and stored at -10 °C until analysis, usually within 1 week. Reaction products were analyzed for the ratio of toluene to toluene-α-*d* by using either GC/MS or high-resolution mass spectrometry (KRATOS MS-50). In the latter case, toluene was separated and collected on a gas chromatograph prior to analysis. The entire collected sample was introduced into the mass spectrometer and analyzed at an ionizing voltage of 70 eV with resolution never less than 1:50000.

In a typical experiment, tetralin, triphenylsilane-*d*, dibenzylmercury, and *tert*-butylbenzene were weighed into five microreactors. The weight of triphenylsilane-*d* was kept constant (0.520 g, 2.00 mmol) while that of tetralin was increased from reactor to reactor, providing mole ratios of tetralin to triphenylsilane-*d* of 0.252, 0.504, 1.00, 1.54, and 2.01. The total volume was kept to approximately 2.0 mL by reducing the weight

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