Large Transition State Imbalance in the Expulsion of Arylnitromethane Anions from Aniline Adducts of α-Nitrostilbenes

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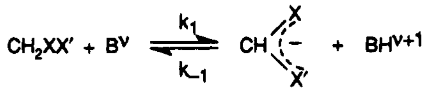
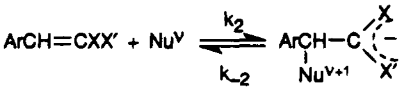
Aniline adducts of α-nitrostilbenes, $PhCH(HNC_6H_4Z)CH(C_6H_4Y)NO_2$ have been synthesized for a variety of Z/Y combinations. In several cases a mixture of two diastereomers was obtained. Structural assignment of the diastereomers was based both on ^1H NMR and reactivity data. The kinetics of the breakdown of the adducts into the respective benzalanilines and arylnitromethane anions was studied in acidic 50% Me_2SO–50% water solutions at 5 °C. The rate constants, k_{exp}, were found to be independent of buffer concentration and pH, indicating a unimolecular mechanism. There is a strong dependence on the aniline substituent ($\varrho = -2.2$) and the pK_a of the arylnitromethanes ($\beta_{lg} = -1.28$). By estimating the substituent dependence of the equilibrium constant (K_{exp}), approximate *normalized* structure–reactivity parameters $\alpha^{n}_{exp} = (\mathrm{dlog}\ k_{exp}/\mathrm{dlog}\ K_{exp})_Z \approx 1.28$ and $\beta^{n}_{exp} = (\mathrm{dlog}\ k_{exp}/\mathrm{dlog}\ K_{exp})_Y \approx 0.58$ have been calculated. This suggests the presence of a substantial transition state imbalance ($\alpha^{n}_{exp} - \beta^{n}_{exp} \approx 0.70$), similar to that in the deprotonation of arylnitromethanes.

We have been interested in the factors that govern reactivity and transition state structures of reactions that lead to the formation of stable carbanions. The study of rates of proton transfers from carbon acids, eq 1, has provided a particularly rich source of relevant data. A major conclusion that has emerged from these studies is that the *intrinsic* rate constant, k_o ($k_o = k_1 = k_{-1}$ when $K_1 = 1$) decreases with increasing resonance stabilization of the resulting carbanion.[1] The decrease in k_o can be attributed to a lag in the development of resonance at the transition state; this lag is commonly called a transition state imbalance.[1,2] Such imbalances manifest themselves not only in the depressed intrinsic rate constants but also in the Brønsted α_{CH} values (variation of remote substituent in the carbon acid) that typically exceed the Brønsted β_B values (variation of B^v).[3,4] Large imbalances as measured by $\alpha_{CH} - \beta_B$ are typically associated with very low k_o values.



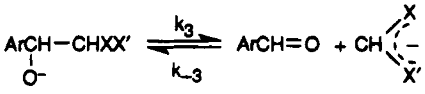
$$CH_2XX' + B^{v} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH\overset{X}{\underset{X'}{\langle}}{}^{-} + BH^{v+1} \qquad (1)$$

Nucleophilic addition to electrophilic alkenes, to form carbanionic adducts, eq 2, show similar decreases in k_o with increasing π-acceptor strength of X and X′ which again can be attributed to an imbalance between charge build-up and charge delocalization at the transition state.[1,7] Here the imbalances have been confirmed by showing that $\alpha^{n}_{nuc} > \beta^{n}_{nuc}$, with $\alpha^{n}_{nuc} = \mathrm{dlog}\ k_1/\mathrm{dlog}\ K_1$ (variation of aryl substituent in alkene) and $\beta^{n}_{nuc} = \mathrm{dlog}\ k_1/\mathrm{dlog}\ K_1$ (variation of Nu^v).

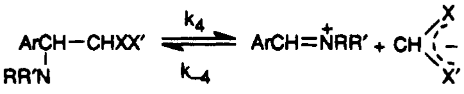


$$ArCH{=}CXX' + Nu^{v} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{Nu^{v+1}}{ArCH}-C\overset{X}{\underset{X'}{\langle}}{}^{-} \qquad (2)$$

Other carbanion-forming reactions that are of considerable interest but for which only few relevant data are available are shown in eqs 3 and 4. Estimates of k_o for eq 3 with XX′ = $(CN)_2$,[8] $C_6H_4(CO)_2$[8b,9] and H, NO_2,[10] and for eq 4 with XX′ = $(CN)_2$[12] and (CN), C_6H_4-4-NO_2[11] again show a strong inverse correlation between k_o and π-acceptor strength of XX′. What has been more difficult to come by for these reactions is a set of structure–reactivity parameters that would directly probe the imbalance. For example, for eq 3 (X = H, X′ = NO_2) dlog k_3/log K_3 was determined from the dependence on the aryl substituent but no structure–reactivity coefficient could be obtained which would probe the charge distribution on the leaving group. In a study of reaction 5 an approximate $\beta_{lg} = \mathrm{dlog}\ k_5/pK_a^{ArCH_2NO_2}$ was calculated[12] but from this structure–reactivity coefficient alone one cannot evaluate the imbalance.



$$\underset{O^-}{ArCH}-CHXX' \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} ArCH{=}O + CH\overset{X}{\underset{X'}{\langle}}{}^{-} \qquad (3)$$



$$\underset{RR'N}{ArCH}-CHXX' \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} ArCH{=}\overset{+}{N}RR' + CH\overset{X}{\underset{X'}{\langle}}{}^{-} \qquad (4)$$

[⊗] Abstract published in *Advance ACS Abstracts*, August 15, 1994.

(1) (a) Bernasconi, C. F. *Acc. Chem. Res.* **1987**, *20*, 301. (b) Bernasconi, C. F. *Ibid.* **1992**, *25*, 9. (c) Bernasconi, C. F. *Adv. Phys. Org. Chem.* **1992**, *27*, 119.

(2) (a) Jencks, D. A.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 7948. (b) Jencks, W. P. *Chem. Rev.* **1985**, *85*, 511.

(3) For a recent review with numerous examples, see ref 1c.

(4) α_{CH} exceeds β_B whenever the location of the remote substituent (Z) is such as to be closer to the negative charge in the transition state than in the product, e.g., in the deprotonation of Z-$C_6H_4CH_2NO_2$.[5] In cases where Z is closer to the negative charge in the product than in the transition state, e.g., in the deprotonation of triphenyl(2-substituted-9-fluorenyl)phosphonium ions,[6] the lag manifests itself as $\alpha_{CH} < \beta_B$.

(5) Bordwell, F. G.; Boyle, W. J. *J. Am. Chem. Soc.* **1972**, *94*, 3907.

(6) Bernasconi, C. F.; Fairchild, D. E. *J. Phys. Org. Chem.* **1992**, *5*, 409.

(7) Bernasconi, C. F. *Tetrahedron* **1989**, *45*, 4017.

(8) (a) Bernasconi, C. F.; Kanavarioti, A.; Killion, R. B., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 3612. (b) Bernasconi, C. F.; Laibelman, A.; Zitomer, J. L. *Ibid.* **1985**, *107*, 6563.

(9) $CH_2C_6H_4(CO)_2$ = 1,3-indandione.

(10) Bernasconi, C. F.; Paschalis, P. *J. Am. Chem. Soc.* **1989**, *111*, 5893.

(11) Bernasconi, C. F.; Murray, C. J. *J. Am. Chem. Soc.* **1984**, *106*, 3257.

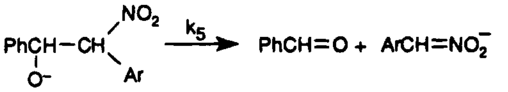
(12) Bernasconi, C. F.; Fassberg, J. *J. Am. Chem. Soc.* **1994**, *116*, 514.

0022-3263/94/1959-5404$04.50/0

Table 1. ^{1}H Chemical Shifts of the 1-(Z,Y) Adducts[a]

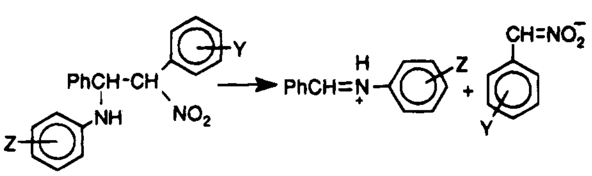
Z	Y	diastereomer	H^{α} [b]	H^{β} [c]	H^{NH} [d]
4-OCH_3	H	B	5.897	5.479	4.918
4-CH_3	H	A	5.898	5.450	4.670
4-CH_3	H	B[e]	5.898	5.541	5.088
H	H	A	5.916	5.492	4.846
4-Cl	H	A	5.905	5.447	4.999
4-CH_3	4-Br	B	5.883	5.484	5.082
H	4-Br	A	5.888	5.440	4.841
H	4-Br	B[e]	5.894	5.528	5.281
4-Cl	4-Br	B	5.894	5.490	5.430
3-NO_2	4-Br	A	5.933	5.537	5.413
3-NO_2	4-Br	B	5.927	5.614	5.887
H	4-NO_2	A[e]	6.058	5.524	4.902
H	4-NO_2	B	6.065	5.579	5.328
4-Cl	4-NO_2	B	6.058	5.541	5.467
3-NO_2	4-NO_2	B	6.107	5.674	5.936

[a] In CD_3CN at 300 MHz. [b] Doublet, $J = 10.8$ Hz. [c] Triplet, $J = 10.5$ Hz. [d] Doublet, $J = 10$ Hz. [e] Minor component.



$$PhCH(O^-)-CH(NO_2)(Ar) \xrightarrow{k_5} PhCH{=}O + ArCH{=}NO_2^- \qquad (5)$$

In this paper we report a kinetic study of the reaction shown in eq 6 and our attempts at estimating the imbalance for this process.

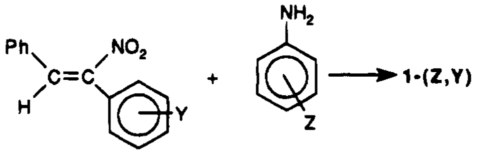


(6)

1-(Z,Y) **2-Z⁺** **3-Y⁻**

Results

Preparation and NMR Spectra of the 1-(Z,Y) Adducts. The **1-(Z,Y)** adducts were prepared either by reaction of the appropriate α-nitrostilbene and aniline, eq 7, or by reaction of arylnitromethane with the appropriate benzalaniline in the presence of diethylamine as a catalyst, eq 8.



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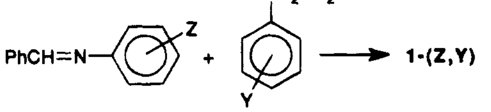

(8)

The following adducts were successfully prepared:

1-(4-MeO,H)
1-(4-Me,H)
1-(H,H)
1-(4-Cl,H)
1-(4-Me,4-Br)
1-(H,4-Br)
1-(4-Cl,4-Br)
1-(3-NO₂,4-Br)
1-(H,4-NO₂)
1-(4-Cl,4-NO₂)
1-(3-NO₂,4-NO₂)

Other Z/Y combinations were attempted but did not yield the desired adducts.

The proton NMR signals of the hydrogens on the α- and β-carbons[13] and the aniline nitrogen are reported in Table 1. The signals for H^{α} and H^{β} appear at δ 5.9–6.1 and δ 5.4–5.7 ppm, respectively, and are coupled with $J_{\alpha\beta} = 10.8$ Hz. The amino hydrogen H^{NH} appears at δ 4.8–6.0 and couples to H^{β} with $J_{\beta\text{-NH}} \approx 10$ Hz. Consequently H^{β} appears as a triplet while H^{α} and H^{NH} appear as doublets.

In several cases there are two sets of signals in the NMR spectrum, which indicates that these samples represent a mixture of diastereomers. This was the case for **1-(4-Me, H)**, **1-(H,4-Br)**, **1-(3-NO₂,4-Br)**, and **1-(H,4-NO₂)**. Except for **1-(3-NO₂,4-Br)**, signals for one diastereomer could readily be distinguished from those of the other by their integration. In the case of **1-(3-NO₂,4-Br)**, where the two isomers were present in approximately equal amounts, the H^{α} and H^{β} resonances that were further downfield were assigned to the diastereomer with the largest shift for H^{NH} (isomer B). This assignment is consistent with the shifts observed for the two forms of **1-(4-Me,H)**, **1-(H,4-Br)** and **1-(H,4-NO₂)**. The procedures used to distinguish between the A and B isomers in those cases where there is only one diastereomer will be dealt with in the Discussion.

It should be noted that some adducts were not stable and decomposed gradually to the corresponding arylnitromethane and benzalaniline in the NMR tube. In the case of **1-(H,H)** the NMR spectrum initially showed signals for just one isomer. However, over time signals for the other diastereomer appeared at the expense of the original signals, ultimately giving a mixture of diastereomers.

Breakdown of 1-(Z,Y). A. Qualitative Observations. Figure 1 shows a series of UV spectra for a solution of **1-(H,H)** in 0.002 M HCl in 50% Me_2SO–50% water at 5 °C. There is a relatively rapid appearance of an absorption maximum at 277 nm (Figure 1A) which subsequently decays on a slower time scale (Figure 1B). Similar behavior is observed throughout the pH range ~1 to 5.75 using a variety of buffered and nonbuffered solutions, although the rates of the two processes vary. The first process is generally too fast to observe at room temperature, but is measurable at 5 °C.

These observations can be understood with reference to Scheme 1. The breakdown of **1-(Z,Y)** yields the protonated benzalaniline (**2-Z⁺**) and the phenylnitromethane anion (**3-Y⁻**) as immediate products. However, in the pH range studied, benzalaniline ($\lambda_{max} = 272$ nm, shoulder at 306 nm)[14] is hydrolyzed to aniline and benzaldehyde very rapidly and thus the observed spectra cannot be due to benzalaniline. The phenylnitromethane anion has a strong absorbance at 303 nm[15] and therefore is also not responsible for the observed absorbance at 277 nm. However, phenylnitronate ions are known to undergo rapid oxygen protonation to form the nitronic acid (**3-Y$_{OH}$**); for Y = H, $pK_a^{NOH} = 4.77$ and $\lambda_{max} = 277$ nm in 50% Me_2SO–50% water at 20 °C.[15] Hence the observed increase in absorbance at 277 nm must be due to the formation of the nitronic acid. The subsequent disappearance of this absorption corresponds to the tautomerization of **3-Y$_{OH}$** into the thermodynamically more stable **3-Y$_{CH}$** which has no significant absorption above 260 nm. In accordance with this interpretation, addition of a solution of phenylnitromethane anion to an HCl solution

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[13] The α-carbon is the one with the nitro group, the β-carbon the one with the aniline moiety.

[14] *Handbook of Chemistry and Physics*, 56th ed., Weast, R. C., Ed.; CRC Press: Cleveland, OH, 1975.

[15] Bernasconi, C. F.; Kliner, D. A. V.; Mullin, A. S.; Ni, J. X. *J. Org. Chem.* **1988**, *53*, 3342.

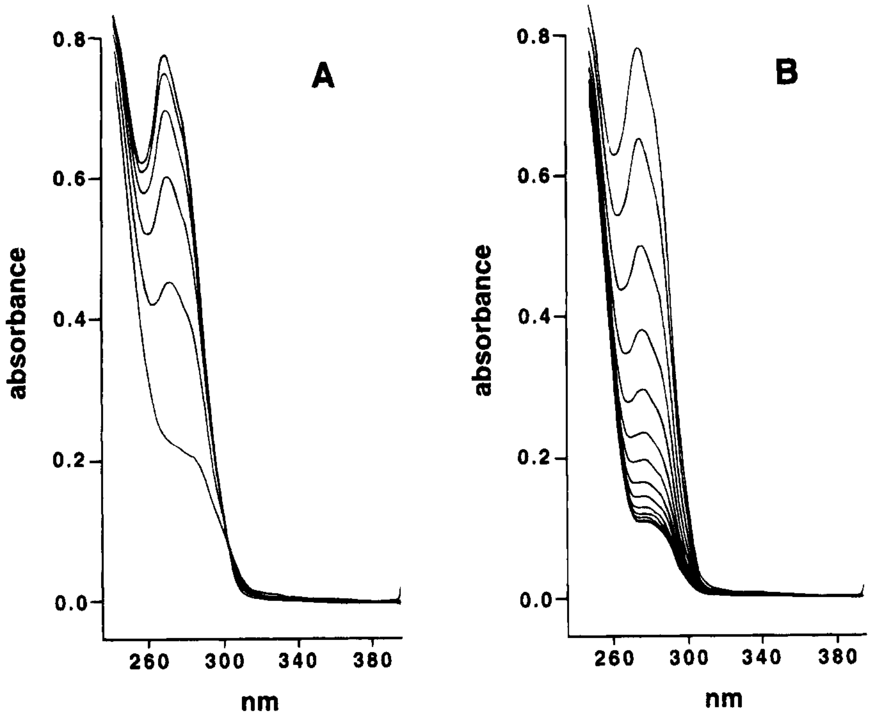
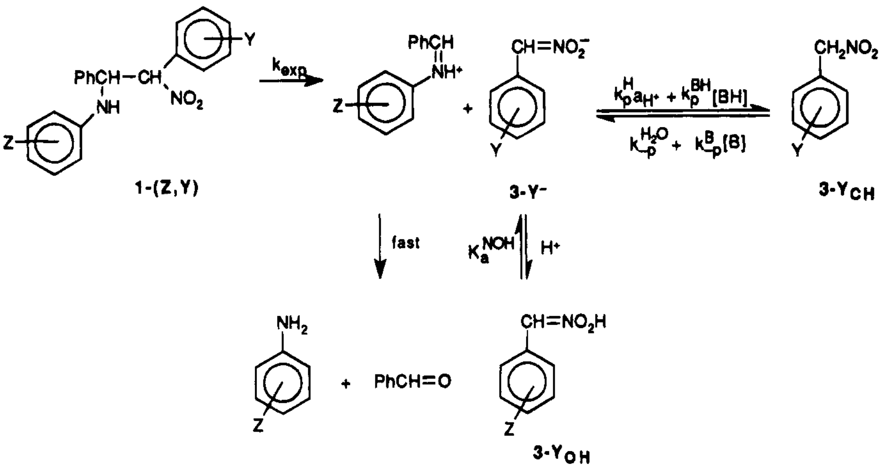


Figure 1. UV spectra of a ca. 4.7 × 10^{-5} M solution of **1-(H,H)** in 0.002 M HCl in 50% Me_2SO–50% water at 5 °C. (A) Process of increasing absorbance, 2 min intervals. (B) Process of decreasing absorbance, 10 min intervals.

Scheme 1



gives an absorbance at 277 nm which decays at the same rate as in the experiment shown in Figure 1B.

B. Kinetic Measurements in HCl Solutions. The qualitative features described above indicate that the kinetic scheme we are dealing with is that of eq 9. k_{exp} refers to the unimolecular expulsion of the arylnitromethane anion from **1-(Z,Y)**; in a pH range where the NH-group of **1-(Z,Y)** is not significantly protonated and the α-carbon is not significantly deprotonated, this process should be pH-independent.[16] k_{taut} refers to the tautomerization of **3-Y$_{OH}$** via **3-Y$^-$** and is given by eq 10, with K_a^{NOH} being the acid dissociation constant of **3-Y$_{OH}$**.

$$1\text{-}(Z,Y) \xrightarrow{k_{exp}} 3\text{-}Y_{OH} \xrightarrow{k_{taut}} 3\text{-}Y_{CH} \tag{9}$$

$$k_{taut} = k_p^H a_{H^+} \frac{K_a^{NOH}}{K_a^{NOH} + a_{H^+}} \tag{10}$$

In HCl solutions at pH < 3, $K_a^{NOH} \ll a_{H^+}$[15] and hence eq 10 simplifies to eq 11, i.e., k_{taut} should also be pH-independent.

$$k_{taut} = k_p^H K_a^{NOH} \tag{11}$$

The kinetic measurements were carried out in 0.002 M and 0.10 M HCl in 50% Me_2SO–50% water at 5 °C. The results, which are summarized in Table 2, show that between pH 1.0 and 2.7 k_{exp} and k_{taut} are, within experimental error, pH-independent, indicating that **1-(Z,Y)** is not significantly ionized and confirming the validity of eq 11.[18] The evaluation of k_{exp} and k_{taut} was

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(16) The basicity of the NH group in **1-(Z,Y)** is expected to be substantially lower than that of aniline (pK_a = 4.25 in 50% Me_2SO–50% water),[17] because of the electron-withdrawing effect of the phenyl and $CH(NO_2)Ar$ groups attached to the nitrogen. The acidity of the CH group α to the nitro group in **1-(Z,Y)** is expected to be slightly higher than that of phenylnitromethane (pK_a = 7.95 in 50% Me_2SO–50% water).[15]

Table 2. Observed Rate Constants for the Decomposition of 1-(Z,Y) Adducts and the Subsequent Tautomerization of 3-Y_{OH} in HCl Solutions in 50% Me_2SO–50% H_2O at 5 °C[a]

Z	[HCl] M	$10^3 k_{exp}$ s^{-1}	$10^3 k_{taut}$ s^{-1}	k_{exp}/k_{taut}
		1-(Z,H)		
4-OMe	0.002	3.5	0.63	5.6
	0.10	3.1	0.64	4.9
4-Me	0.002	~7.8[b]	0.61	13
	0.10	~7.1[b]	0.60	12
H	0.002	2.7	0.60	4.5
	0.10	2.6	0.61	4.3
4-Cl	0.002	1.1[d]	0.49[d]	2.2
	0.10	1.0[d]	0.51[d]	2.0
k_{taut}[c]	0.002		0.64	
	0.10		0.63	
		1-(Z,4-Br)		
4-Me	0.002	5.0	1.4	3.6
	0.10	5.1	1.4	3.6
H	0.002	~5.3[b]	1.4	3.8
	0.10	~6.3[b]	1.3	4.8
4-Cl	0.002	0.50	1.5	0.33
	0.10	0.50	1.4	0.36
3-NO_2	0.002	0.21; 0.066[f]		
	0.10	0.22; 0.063[f]		
k_{taut}[c]	0.002		1.37	
	0.10		1.37	
		1-(Z,4-NO_2)		
H	0.002	38	13	2.9
	0.10	53	16	3.3
4-Cl	0.002	20[d]	10[d]	2.0
	0.10	26[d]	11[d]	2.4
3-NO_2	0.002	1.4	20	0.070
	0.10	1.5	23	0.065
k_{taut}[c]	0.002		14.4	
	0.10		16.5	

[a] μ = 0.5 M (KCl). [b] Curved log plot, due to reaction of two diastereomers, see text. [c] Determined independently in a solution containing only **3-Y_{OH}**. [d] Assignment of the higher value to k_{exp} and the lower value to k_{taut} is tentative, see text. [e] Triphasic kinetics, k_{taut} not evaluated; the two k_{exp} values refer to the two diastereomers, see text.

not straightforward for all Z,Y-combinations. One problem was that in some cases the two kinetic processes were not well separated (ratio of rate constants less than 3) which renders the rate constants relatively inaccurate, especially those referring to the faster reaction.[19] This is particularly true for **1-(4-Cl,H)** and **1-(4-Cl,4-NO_2)** where, because of the small ratios, the assignment of the rate constants to their respective process may be questionable. This problem could not be circumvented by monitoring the decay of **1-(Z,Y)** which would yield an accurate k_{exp}, the rate constant of main interest; this is because **3-Y_{OH}** rather than **1-(Z,Y)** is the absorbing species in eq 9.

A second problem was that with **1-(4-Cl,4-Br)**, **1-(3-NO_2,4-Br)**, and **1-(3-NO_2,4-NO_2)** the usual assignment of the fast process to k_{exp} and of the slow process to k_{taut} had to be reversed, i.e., here $k_{exp} < k_{taut}$. This reversal was confirmed by direct measurement of k_{taut} for the corresponding arylnitromethane anions under the same reaction conditions; these directly measured k_{taut} values are included in Table 2.

The third problem is that with **1-(4-Me,H)** and **1-(H,4-Br)** the fast process does not obey clean first-order kinetics but is biphasic.[20] This can be attributed to the fact that these adducts are mixtures of diastereomers which have different k_{exp} values. The difference in the k_{exp} values between the two diastereomers is too small to allow separate determination of both rate constants and hence the values reported in Table 2 represent weighted averages of the two. Note that a similar situation exists for **1-(3-NO_2,4-Br)** except that in this case $k_{exp} < k_{taut}$. Hence the two processes being the two slowest ones of a total of three could be resolved to yield separate rate constants for the two diastereomers.[21]

C. Kinetic Measurements in Buffered Solutions. The problems due to poor separation and multiple diastereomers could both be overcome by exploiting the fact that k_{taut} can be substantially enhanced in the presence of carboxylate buffers. This buffer dependence is due to rate limiting protonation of **3-Y^-** to give **3-Y_{CH}**, i.e., in the presence of a buffer, eq 10 becomes eq 12, and eq 11 becomes eq 13.

$$k_{taut} = (k_p^H a_{H^+} + k_p^{BH}[BH])\frac{K_a^{NOH}}{K_a^{NOH} + a_{H^+}} \tag{12}$$

$$k_{taut} = \{k_p^H + k_p^{BH}([BH]/a_{H^+})\}K_a^{NOH} \tag{13}$$

This method was used for the substrates **1-(4-Cl,H)**, **1-(4-Cl,4-NO_2)**, **1-(H,4-NO_2)**, **1-(4-Me,H)**, and **1-(H,4-Br)** for which the results in HCl solution are ambiguous or less than satisfactory. The new data are reported in Table 3. For **1-(4-Cl,H)** and **1-(4-Cl,4-NO_2)** the increase in k_{taut} changes the k_{exp}/k_{taut} ratio from approximately 2 in HCl solution to as low as 0.12 for **1-(4-Cl,H)** and to 0.18 for **1-(4-Cl,4-NO_2)** in the buffer. Hence the larger separation and the fact that k_{exp} refers now to the slower process greatly enhance the precision with which k_{exp} can be obtained. A potential drawback of experiments where the k_{exp}/k_{taut} ratio is substantially smaller than unity is that the nitronic acid never reaches a concentration level even approaching that of $[\mathbf{1\text{-}(Z,Y)}]_o$. This problem was overcome by using relatively high $[\mathbf{1\text{-}(Z,Y)}]_o$ to ensure reasonably large absorbance values.

For **1-(4-Me,H)**, **1-(H,4-Br)**, and **1-(H,4-NO_2)** the advantage of using buffered solutions was not so much to increase the separation between k_{exp} and k_{taut} (in fact the separation becomes smaller) but to reverse the k_{exp}/k_{taut} ratio from >1 to <1 so that k_{exp} would become the more accurately measurable rate constant and, for **1-(4-Me,H)** and **1-(H,Br)**, k_{exp} could be more easily resolved in terms of two processes for the two stereoisomers (k_{exp} and k'_{exp}). Where the values obtained in the buffered solutions differed from those obtained in the HCl solutions, the former were judged to be more reliable.

Discussion

NMR Data and Correlation of Stereochemistry. Inspection of the proton NMR data in Table 1 reveals that when there is a mixture of two diastereomers, the shifts of H^{NH} of one diastereomer is approximately 0.4 ppm downfield from that of the other. It is reasonable

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[17] Bernasconi, C. F.; Carré, D. J.; Fox, J. P. In *Techniques and Applications of Fast Reactions in Solution*; Gettins, W. J., Wyn-Jones, E., Eds.; Reidel: Dordrecht, Holland, 1979; p 453.

[18] Since the assumptions leading to eq 11 were based on pK_a^{NOH} data at 20 °C, it is important to show that our results confirm the validity of eq 11 at 5 °C.

[19] Bernasconi, C. F. *Relaxation Kinetics*; Academic Press: New York, 1976; Chapter 9.

[20] The reaction is triphasic overall.

[21] In biphasic or triphasic kinetic plots that are not well separated the rate constant(s) referring to the slowest phase(s) can generally be determined with better accuracy than those of the fastest phase.[19]

Table 3. Observed Rate Constants for the Decomposition of Selected 1-(Z,Y) Adducts and the Subsequent Tautomerization of 3-Y_{OH} in Carboxylate Buffers in 50% Me_2SO–50% Water at 5 °C[a]

pH[b]	[BH] M	[B^-] M	$10^3 k_{exp}$ s^{-1}	$10^3 k'_{exp}$[c] s^{-1}	$10^3 k_{taut}$ s^{-1}
			1-(4-Cl,H)		
3.41	0.02	0.01	0.70		3.07
3.41	0.04	0.02	0.67		5.70
3.41	0.06	0.03	0.67		
3.41	0.10	0.05	0.66		
3.41	0.20	0.10	0.69		
			1-(4-Cl,4-NO_2)		
1.85	0.08	0.04	13.1		71.6
1.85	0.12	0.06	13.3		
1.85	0.20	0.10	13.5		
2.15	0.02	0.02	13.5		38.1
2.15	0.04	0.04	12.8		66.5
2.15	0.10	0.10	13.9		
			1-(H,4-NO_2)		
2.15	0.06	0.06	37.6		100
2.15	0.08	0.08	41.8		106
2.15	0.10	0.10	40.0		
2.15	0.20	0.20	42.5		
2.15	0.30	0.30	42.4		
			1-(4-Me,H)		
3.41	0.12	0.06	6.6	1.4	*d*
3.41	0.20	0.10	6.7	1.2	*d*
			1-(H,4-Br)		
2.15	0.20	0.20	6.8	1.5	13[e]
2.15	0.30	0.30	5.8	1.4	19[e]
3.41	0.16	0.08	8.0	1.7	*d*
3.41	0.20	0.10	7.9	1.9	*d*

[a] μ = 0.5 M (KCl). [b] BH = Chloroacetic acid for pH 3.41, dichloroacetic acid for pH 1.85 and 2.15. [c] Decomposition of second diastereomer. [d] Not measurable with sufficient accuracy. [e] Measured independently in solution only containing **3-Y_{OH}**.

to assume that the isomers with the H^{NH} signal further upfield share comparable stereochemistry; we have arbitrarily designated this configuration as A and that with the H^{NH} signal further downfield as B.

Shifts of amino hydrogens of substituted anilines commonly correlate with the Hammett σ-constants.[22,23] Hence it is reasonable to expect that the shift of H^{NH} will fall on a Hammett line for diastereomers with the same configuration. Furthermore, we would expect the ϱ-values to be similar for all Hammett series. On the basis of these assumptions, we can use the Hammett correlations to establish the configurations of those adducts that are only present in one configuration, i.e., as either A or B.

Figure 2 shows Hammett plots of the chemical shift of H^{NH} vs σ of the Y-substituent. In order to evaluate ϱ we consider **1-(H,4-Br)** and **1-(H,4-NO_2)**, for which NMR data is available for both isomers. The Hammett line through the B diastereomers gives a slope of 0.085 ppm/σ; a line of similar slope can be drawn through the two points of the A diastereomers.

Based on the assumption that the ϱ-values of each series should be similar, the configuration of the remaining adducts are determined from the Hammett plots as follows.

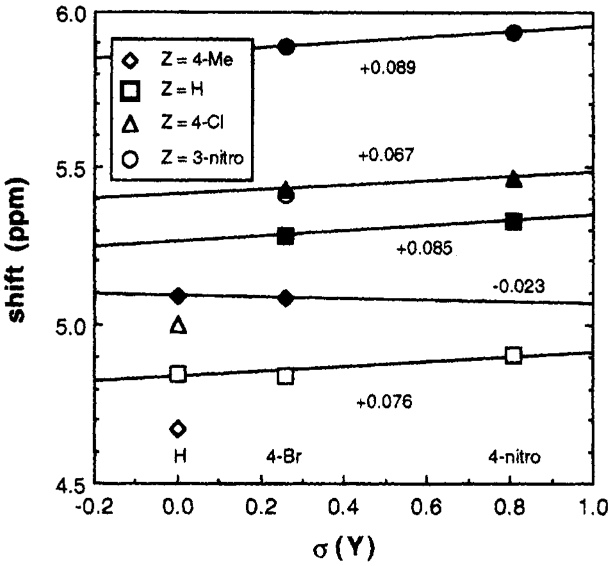

Figure 2. Hammett plots of the H^{NH} shift vs σ of the Y-substituent in CD_3CN. Open symbols correspond to diastereomer A, filled symbols to diastereomer B.

(1) The point for **1-(H,H)** falls very close to the line defined by the A diastereomers but far from that defined by the B diastereomers. Hence the configuration of **1-(H,H)** corresponds to diastereomer A.

(2) A line of slope 0.089 can be drawn through the points for **1-(3-NO_2,4-NO_2)** and the B form of **1-(3-NO_2,4-Br)** establishing the configuration of the former as B.

(3) **1-(4-Me,4-Br)** clearly has the B configuration, since its point falls close to a line of slope 0.1 (not shown) drawn through the point for the B form of **1-(4-Me,H)**. The slope of the line through these points is −0.023; given the scatter of the data and the close spacing of these two points, this slope is not significantly different from 0.1.

(4) The line drawn through the points of **1-(4-Cl,4-Br)** and **1-(4-Cl,4-NO_2)** has a slope of 0.067 and passes 0.4 ppm above the point for **1-(4-Cl,H)**. Hence **1-(4-Cl,4-Br)** and **1-(4-Cl,4-NO_2)** share the B configuration, while **1-(4-Cl,H)** has the A configuration.

By this process, the configurations are established for all the adducts except **1-(4-OMe,H)**. However, its configuration is readily determined from the Hammett plot of shift vs σ of the Z-substituent (Figure 3) by analogous reasoning. It clearly has the B configuration, since its point lies well above the Hammett line defined by the A diastereomers, but close to a line of the same slope passing through the B form of **1-(4-Me,H)**.

A question of considerable interest is which diastereomer corresponds to the A, and which to the B configuration. The larger downfield shift of the amino proton in the B form is consistent with a greater degree of intramolecular hydrogen bonding between this hydrogen and the nitro group than is the case for the A form. Models and Newman projections suggest that intramolecular hydrogen bonding should favor diastereomer **4** because both diastereomers should prefer a conformation in which the α and β aryl groups are anti to each other. In **4** this arrangement (**4a**) places the nitro and amino groups gauche, allowing hydrogen bonding between them. In **5**, however, when the α and β aryl groups are anti (**5a**), the amino and nitro groups are also anti to each other.

If this interpretation is correct, diastereomer B corresponds to **4** and its enantiomer. The intramolecular hydrogen bonding should render B more stable thermodynamically, which is consistent with a slower rate of

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[22] (a) Buncel, E.; Webb, J. G. K. *Can. J. Chem.* **1974**, *52*, 630. (b) Lynch, B. M.; MacDonald, B. C.; Webb, J. G. K. *Tetrahedron* **1968**, *24*, 3595.

[23] (a) Yonemoto, T.; Reynolds, W. F.; Hutton, H. M.; Schaeffer, T. *Can. J. Chem.* **1965**, *43*, 2668. (b) Dyall, K. *Aust. J. Chem.* **1964**, *17*, 419.

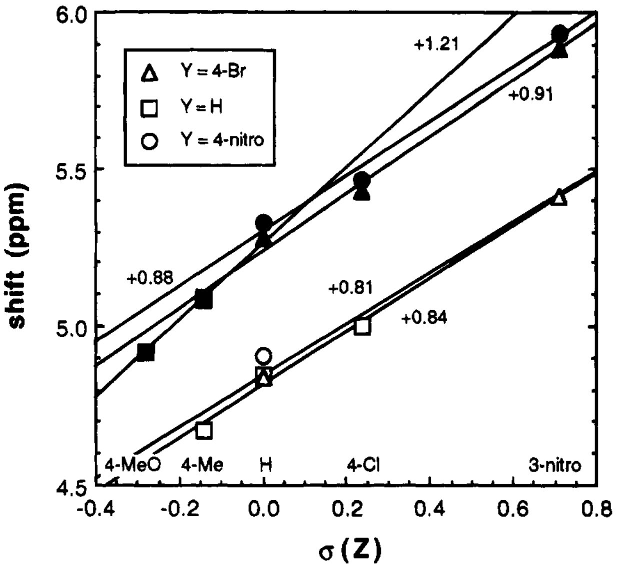
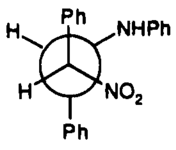
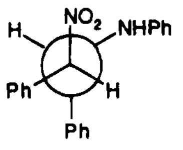


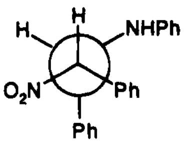
Figure 3. Hammett plots of the H^{NH} shift vs σ of the Z-substituent in CD_3CN. Open symbols correspond to diastereomer A, filled symbols to diastereomer B.



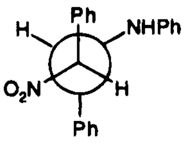
4a



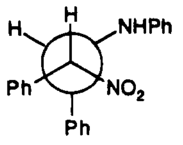
4b



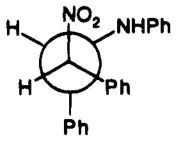
4c



5a



5b



5c

collapse (see below) and with the observation that **1-(H,H)** is gradually converted from A to B in $CDCl_3$.

Kinetic Results. Average values of k_{exp} for all adducts are summarized in Table 4. The error limits for k_{exp} are estimated at ±25%. The relatively large uncertainty is primarily due to the relatively small separation between the various kinetic processes, especially the uncertainty in resolving the contribution from the two diastereomers of the **1-(Z,Y)** adducts.

For several adducts, k_{exp} values are available for both diastereomers; these differ by a factor of 3–5. It is not immediately obvious which rate constant applies to which diastereomer, but since we expect like diastereomers to fall on the same Hammett line, this problem can be solved by comparing k_{exp} values with those for adducts of known configuration, as described below.

Dependence on the Aniline Substituent (Z). Hammett plots of log k_{exp} vs σ for the Z-substituent are shown in Figure 4. A set of essentially parallel lines can be drawn as follows.

For Y = NO_2, all three experimental points (corresponding to the B isomer) clearly lie on one line with $\varrho = -2.07$ ($r = 0.999$). Also, k_{exp} was obtained for both **1-(H,4-Br)** and **1-(3-NO$_2$,4-Br)** for both diastereomers. The isomers with the smaller k_{exp} values correlate well ($\varrho = -2.15$, $r = 0.993$) with **1-(4-Me,4-Br)** and **1-(4-Cl,4-Br)**, indicating that they share the B configuration. The larger rate constants for **1-(H,4-Br)** and **1-(3-NO$_2$,4-Br)** must therefore correspond to the A isomer; the Hammett line through these two points yields $\varrho = -2.15$.

Table 4. Summary of the Average Rate Constants k_{exp} for the Decomposition of the 1-(Z,Y) Adducts in 50% Me_2SO–50% Water at 20 °C[a,b]

Z	diastereomer[c]	Y = H	Y = 4-Br	Y = 4-NO_2
4-OCH_3	B	3.3×10^{-3}		
4-CH_3	A	6.6×10^{-3}		
	B	1.3×10^{-3}	5.0×10^{-3}	
H	A	2.6×10^{-3}	7.1×10^{-3}	
	B		1.6×10^{-3}	4.1×10^{-2}
4-Cl	A	7.0×10^{-4}		
	B		5.0×10^{-4}	1.35×10^{-2}
3-NO_2	A		2.1×10^{-4}	
	B		6.4×10^{-5}	1.4×10^{-3}

[a] k_{exp} in units of s^{-1}. [b] μ = 0.5 M (KCl). [c] For assignment of diastereomers, see text.

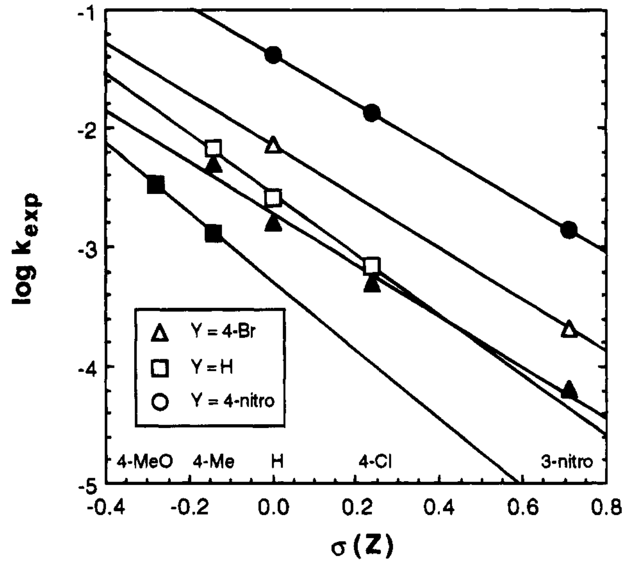


Figure 4. Hammett plots of log k_{exp} vs σ of the Z-substituent. Open symbols correspond to diastereomer A, filled symbols to diastereomer B.

Table 5. Hammett ϱ-Values Based on Varying the Z-Substituent for the Decomposition of 1-(Z,Y)

Y	diastereomer	ϱ	r[a]
H	A	−2.54	0.998
	B	−2.89[b]	NA
4-Br	A	−2.15	NA
	B	−2.15	0.993
4-NO_2	B	−2.07	0.999
average		−2.23	

[a] Correlation coefficient. [b] Based on two closely spaced points, not included in calculation of average.

It is reasonable to expect similar ϱ values for the remaining series, and indeed, the larger and smaller rate constants for **1-(4-Me,H)** can be assigned to the A and B diastereomers, respectively, to give approximately parallel Hammett lines with ϱ values of −2.54 and −2.89. Note, however, that these points span a small range of σ(Z) values, so that these ϱ values are less certain than those for Y = 4-NO_2 and Y = 4-Br.

The various ϱ values are summarized in Table 5. Omitting ϱ for diastereomer B of Y = H, which is based on two closely spaced points, we obtain an average ϱ(Z) value of −2.2. The above analysis shows that the A diastereomers are more reactive than the B diastereomers by a factor of 3–5 which is consistent with the assignment of A to **5** and B to **4**, as discussed earlier.

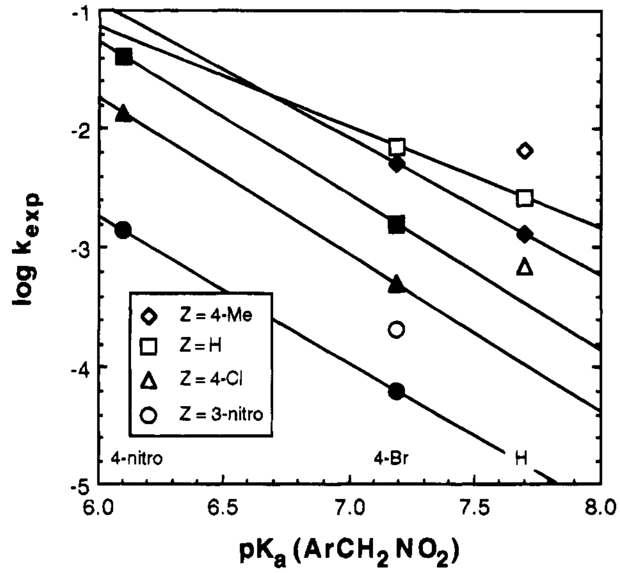


Figure 5. Brønsted-type plot of log k_{exp} vs the pK_a of arylnitromethanes. Open symbols correspond to diastereomer A, filled symbols to diastereomer B.

Table 6. Brønsted β_{lg} Values Based on Varying the Y-Substituent for the Decomposition of 1-(Z,Y)

Z	diastereomer	β_{lg}
4-Me	B	−1.15[a]
H	A	−0.86[a]
	B	−1.29
4-Cl	B	−1.31
4-NO2	B	−1.23
average		−1.28

[a] Based on two closely spaced points, not included in calculation of average.

Dependence on the Arylnitromethane Substituent (Y). Determination of ϱ values from the dependence on σ(Y) is difficult to do with confidence because it is not clear whether the data should be plotted vs σ or σ^-. The pK_a's of arylnitromethanes correlate with σ^- in water[5] but in 50% Me_2SO−50% water they correlate about equally well with σ and σ^-(plot not shown). In view of this uncertainty we have plotted log k_{exp} directly against the pK_a's of the corresponding arylnitromethanes in 50% Me_2SO−50% water at 20 °C.[24] These Brønsted plots are shown in Figure 5.

There are five sets of data through which Brønsted lines can be drawn. Four of these have similar slopes, while the slope for the A form of Z = H is somewhat smaller than that for the other four. But this line, along with one of the others, is based on two closely spaced data points which contain considerable uncertainty, so the discrepancy is within experimental error. The values for all the slopes, $\beta_{lg} = d\log k_{exp}/dpK_a^{CH}$, are summarized in Table 6. If we omit the lines for the A form of Z = H and the B form of Z = Me, which are based on two closely spaced points, we obtain an average $\beta_{lg} = -1.28$.

Constancy of the Structure–Reactivity Coefficients. Our results indicate that the ϱ(Z) values are essentially independent of the Y-substituent in the leaving group and that β_{lg} is independent of the Z-substituent in the aniline moiety. This implies a p_{xy} coefficient[2] that is approximately zero and suggests that there is little, if any, change in the transition state structure as the substituents are varied. This constancy of the structure–reactivity coefficients is reminiscent of the situation in the deprotonation of 1-aryl-1-nitroethanes by amines.[5] It is consistent with reactions that have low intrinsic rate constants or high intrinsic barriers and hence are characterized by energy surfaces with strong curvature at the transition state.[26,27]

Imbalance. So far we have only considered the effect of substituents on the *kinetics* of carbanion expulsion. In order to estimate the imbalance, the ϱ and β_{lg} values need to be normalized, i.e., we also need to know the substituent effects on the *thermodynamics* of the reaction. Since carbanion expulsion from **1-(Z,Y)** is essentially irreversible under our conditions, the substituent effect on the equilibrium constant, K_{exp}, must be estimated.

For the dependence of K_{exp} on Y we shall assume that it parallels the dependence of the acidity (K_a^{CH}) of arylnitromethane on Y, i.e., $d\log K_{exp}/dY \approx d\log K_a^{CH}/dY$, which means $\beta_{eq} = d\log K_{exp}/d\log K_a^{CH} \approx 1$. This is a reasonable assumption, because both the cleavage of **1-(Z,Y)** and the deprotonation of arylnitromethane yield the arylnitromethane anion (**3-Y⁻**) and thus the substituent effects on the two processes should be very similar. Hence, if we define a normalized structure–reactivity coefficient for the dependence on Y as $\alpha_{exp}^n = (d\log k_{exp}/d\log K_{exp})_Z$ we obtain $\alpha_{exp}^n \approx -\beta_{lg}/\beta_{eq} = 1.28$.

For the dependence on Z, the normalized structure-reactivity coefficient is defined as $\beta_{exp}^n = (d\log k_{exp}/d\log K_{exp})_Y = \varrho(k_{exp})/\varrho(K_{exp})$. We shall approximate $\varrho(K_{exp})$ with $\varrho(pK_a^{NH+})$, with pK_a^{NH+} referring to the anilines. Since both the expulsion reaction and the protonation of anilines require placing a positive charge on the aniline nitrogen, this approximation is reasonable. The model is not ideal, though, because the expulsion requires rehybridization of the nitrogen atom while protonation does not. The value for $\varrho(pK_a^{NH+})$ in 50% Me_2SO−50% water, evaluated from the pK_a's of the conjugate acids of aniline (4.25)[17] and 3-nitroaniline (1.55)[28] is −3.8. Thus $\beta_{exp}^n \approx -2.2/-3.8 = 0.58$.

In combination with α_{exp}^n we can now evaluate an approximate imbalance $\alpha_{exp}^n - \beta_{exp}^n \approx 1.28 - 0.58 = 0.70$. In view of some uncertainty in the kinetic data that affect β_{lg} and ϱ(Z), but more importantly, in view of the approximations involved in estimating the substituent effects on the equilibrium constants (β_{eq} and $\varrho(K_{exp})$), the margin of error in α_{exp}^n and β_{exp}^n and thus in the imbalance is quite large. A conservative estimate of the uncertainty in $\alpha_{exp}^n - \beta_{exp}^n$ is ±0.25. Even with this large margin of error, our results clearly demonstrate the presence of a substantial imbalance in this reaction. The imbalances in two other arylnitromethane anion-forming reactions (proton transfer as in eq 1 and nucleophilic addition as in eq 2) are shown in Table 7 for comparison. Because of the large uncertainty in the imbalance for arylnitromethane anion expulsion from **1-(Z,Y)**, firm quantitative conclusions cannot be drawn from the comparison with the other imbalances; differences in solvent and temperature further add to the uncertainties.

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[24] The pK_a values in 50% Me_2SO−50% water at 20 °C for Y = H, 4-Br, 3-NO2, and 4-NO2 are 7.93,[15] 7.43,[25] 6.74[25] and 6.33,[25] respectively.

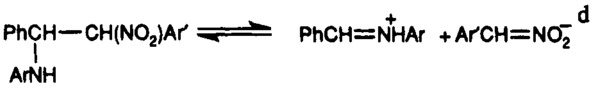
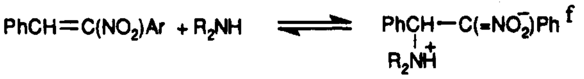
[25] Bernasconi, C. F.; Kittredge, K. W. Unpublished results.

[26] Murray, C. J.; Jencks, W. P. *J. Am. Chem. Soc.* **1990**, *112*, 1880.

[27] For proton transfers from carbon acids that lead to carbanions with less resonance stabilization and thus have lower intrinsic barriers, the transition state *does* change along with changes in substituents of the base and the carbon acid ($p_{xy} > 0$).[6,26]

[28] This work, see Experimental Section.

Table 7. Normalized α and β Values and Imbalances for Arylnitromethane Anion-Forming Reactions

Reaction	α	β	α − β
$ArCH_2NO_2 + R_2NH \rightleftharpoons ArCH{=}NO_2^- + R_2NH_2^+$ [a]	1.29[b]	0.55[b] (0.44)[c]	0.74[b] (0.85)[c]
 $PhCH(NHAr){-}CH(NO_2)Ar' \rightleftharpoons PhCH{=}\overset{+}{N}HAr + Ar'CH{=}NO_2^-$ [d]	~1.28[e]	~0.58[e]	~0.70[e]
 $PhCH{=}C(NO_2)Ar + R_2NH \rightleftharpoons PhCH(\overset{+}{N}HR_2){-}C({=}NO_2^-)Ph$ [f]	~0.67[g]	~0.37[g]	~0.30[g]

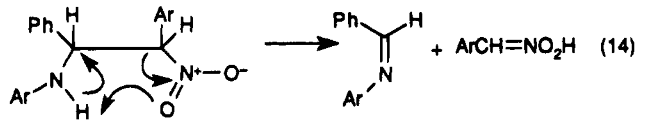
[a] In water at 25 °C, R_2NH = piperidine, piperazine, and morpholine; β determined from reactions with $ArCH(CH_3)NO_2$, ref 5. [b] $\alpha = \alpha_{CH}$, $\beta = \beta_B$. [c] $\beta = 0.44$ based on R_2NH = piperidine and morpholine determined from reaction with $PhCH_2NO_2$. Keeffe, J. R.; Munderloh, N. H. *J. Chem. Soc., Chem. Commun.* **1974**, 17. [d] In 50% Me_2SO–50% water at 5 °C, this work. [e] $\alpha = \alpha^n_{exp}$, $\beta = \beta^n_{exp}$. [f] In 50% Me_2SO–50% water at 20 °C, R_2NH = piperidine and morpholine, ref 29. [g] $\alpha = \alpha^n_{nuc}$, $\beta = \beta^n_{nuc}$.

Nevertheless, it appears that the imbalance for the expulsion reaction, which is of the general type of eq 4, is comparable to that for the proton transfer and definitely larger than that for the nucleophilic addition to α-nitrostilbenes.

It is believed that a major reason why the imbalances in the nucleophilic addition (eq 2) are substantially smaller than in the corresponding proton transfer (eq 1) is that the α-carbon in the olefin does not undergo a change in hybridization.[1,29] This facilitates π-overlap with the nitro group and charge delocalization at the transition state. In contrast, the proton transfer requires that the central carbon be rehybridized from sp^3 to sp^2 in the course of reaction, a feature that adds to the delay in charge delocalization. Steric hindrance by the aryl group of the α-nitrostilbenes, which prevents complete π-overlap with the nitro group, may also contribute to the reduction in the imbalance.[29] An imbalance in reaction 4 that is larger than in reaction 2 but comparable to that in reaction 1 supports this interpretation, since both eqs 4 and 1 involve rehybridization of the central carbon during the reaction.

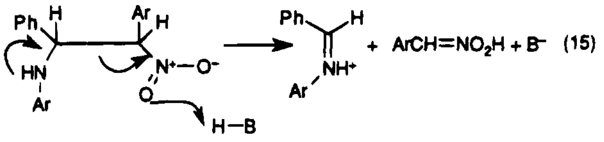
In view of the above-mentioned uncertainties in α^n_{exp} and β^n_{exp}, and also because of the differences in temperature and solvent, we cannot be certain whether the imbalance in the arylnitromethane anion expulsion reaction is essentially the same as for the deprotonation of arylnitromethanes, or whether it is perhaps somewhat smaller. It has been suggested that the imbalance for the proton transfer should be the largest among the carbanion-forming reactions of eqs 1–4 because the transition state for this process is stabilized by hydrogen bonding between the base and the proton being removed.[1a,10,12] This encourages localization of charge on the carbon and should enhance α_{CH}. This notion is supported by the fact that the sensitivity of the intrinsic rate constant to changes in XX′ is larger for proton transfer (eq 1) than for eqs 3 and 4,[1a,10,12] and also by more direct evidence of hydrogen bonding in the transition state of proton transfer.[30,31]

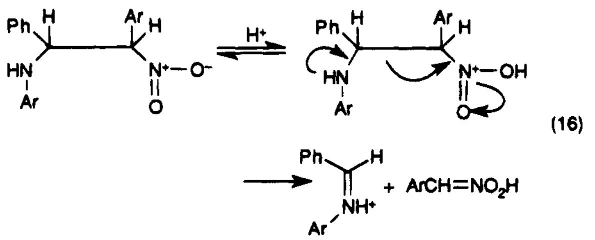
Alternative Reaction Mechanisms. Our entire discussion has been based on the premise that the reaction occurs as shown in Scheme 1. In principle, other mechanistic possibilities exist. One is shown in eq 14 and involves intramolecular proton transfer from the



aniline nitrogen to the nitro group concerted with C—C bond cleavage. This mechanism, which should be characterized by little charge development on the aniline nitrogen and the phenylnitromethane moiety, is ruled out by the fact that ϱ(Z) and β_{lg} are large, indicating a substantial charge build-up on these sites.

Other possibilities are *inter*molecular protonation of the nitro group, either concerted with expulsion (eq 15) which should lead to general acid catalysis, or as rapid preequilibrium (eq 16), which should lead to specific acid catalysis. These mechanisms can be excluded based on the fact that the reaction is independent of buffer concentration and pH.





Conclusions

A major objective of this work has been to obtain structure–reactivity parameters for the breakdown of **1-(Z,Y)** (eq 6) from which one may deduce whether this reaction is subject to an imbalance. Since this reaction is of the type of eq 4 and thus a process that leads to a resonance-stabilized carbanion, an imbalance was expected, but until now no experimental confirmation was

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(29) Bernasconi, C. F.; Renfrow, R. A. *J. Org. Chem.* **1987**, *52*, 3035.
(30) Bednar, R. A.; Jencks, W. P. *J. Am. Chem. Soc.* **1985**, *107*, 7117.
(31) Bernasconi, C. F.; Wiersema, D.; Stronach, M. W. *J. Org. Chem.* **1993**, *58*, 217.

available. The present work shows that there is indeed a substantial imbalance. Despite some uncertainty in the precise numerical value of this imbalance, its magnitude appears to be comparable to that for deprotonation of arylnitromethanes and definitely substantially larger than for nucleophilic addition to α-nitrostilbenes.

Experimental Section

Materials. *p*-Anisidine, *p*-toluidine, 4-chloroaniline, and 3-nitroaniline were recrystallized from ethanol prior to use. Benzaldehyde was washed with aqueous sodium bicarbonate and dried with anhydrous sodium sulfate. Acetonitrile was distilled and stored over molecular sieves. Chloroacetic acid was recrystallized from petroleum ether.

Benzalaniline was prepared according to the method of Bigelow and Eatough[32] and recrystallized from 85% ethanol. The remaining benzalanilines were prepared by mixing equimolar amounts of benzaldehyde and the aniline in 95% ethanol and crystallizing the resulting precipitate from 95% ethanol (benzal-4-chloroaniline, benzal-3-nitroaniline) or hexane (benzal-*p*-toluidine).

The phenylnitromethanes were prepared from the corresponding benzyl bromides by reaction with silver nitrite according to the methods of Kornblum[33] or Avery and Butler.[34]

α-Nitrostilbene was prepared as described by Bordwell and Garbish.[35] KOH and HCl solutions were "Dilut-It" (Baker) diluted to the appropriate volumes with deionized water.

The remaining commercially available products were used without further purification.

Preparation of Aniline-α-Nitrostilbene Adducts. The adducts were prepared according to the methods described by Dornow and Boberg,[36] or by variants thereof. After the reactions were initiated, precipitation of the product, if not spontaneous, was induced by cooling the mixture, adding a nonpolar solvent, seeding with previously prepared material, or a combination of these methods. Since the products are generally not stable, they were typically purified by suspending in hexane to remove residual reactants and ethanol. Melting points are uncorrected. ^{1}H NMR data for the α-CH, β-CH, and NH protons are summarized in Table 1; the aryl protons all appeared between 6.5 and 7.8 ppm (up to 8.2 ppm for **1-(4-Cl,4-NO$_2$)** and **1-(3-NO$_2$,4-NO$_2$)**) and gave the correct integration.[37] All NMR spectra were taken in CD_3CN.

1-(H,H). A suspension of 0.28 g of α-nitrostilbene in approximately 1.5 mL of absolute ethanol was stirred at room temperature. Aniline (0.23 mL, 2 equiv) was added dropwise over approximately 15 s. The liquid deepened in color and the suspended solid dissolved over approximately 1.5 h. The solution was stirred an additional 10 min and then cooled with dry ice–acetone for 5 min to initiate crystallization. After a few small crystals had formed, the reaction mixture was placed in a freezer for 1.5 days, during which a pale yellow precipitate formed. This was filtered off and washed with cold ethanol to yield 0.28 g (71%) of a pale yellow powder, mp 116–119 °C dec (browning above 110 °C) (lit.[36] 123–124 °C dec).

1-(4-Me,H). Preparation 1. To a stirring suspension of 0.20 g of α-nitrostilbene in 2 mL of petroleum ether was added 0.113 g (1.2 equiv) of *p*-toluidine. After stirring for 30 min the solids were gone and a yellow oil had formed. A few drops of diethyl ether were added to dissolve the oil, and the solution was stirred with gentle warming for 4 days, over which a precipitate formed. This product was filtered off and washed with petroleum ether till slightly off-white to afford 92 mg (31%), mp 91–95 °C dec (lit.[36] 110 °C dec). Preparation 2. To a stirring suspension of 0.19 g of α-nitrostilbene in 2 mL of petroleum ether was addéd 0.181 g (2 equiv) of *p*-toluidine. After stirring for 1 min the solids were gone and a reddish oil had formed. Sufficient ethanol was added to dissolve the oil, and the solution was stirred for several minutes more. The solution was then seeded with several grains of the product from preparation 1. The mixture was stirred another 30 min, during which precipitation of additional product was evident. The mixture was then placed in a freezer overnight, after which the product was filtered off and washed with hexanes to give 0.209 g (75%) of slightly off-white powder, mp 96–104 °C dec (lit.[36] 110 °C dec).

1-(4-OMe,H). A suspension of 0.28 g of α-nitrostilbene in approximately 1 mL of absolute ethanol was stirred at room temperature. To this was added 0.153 g (1 equiv) of *p*-anisidine. The reaction mixture turned red as the solids dissolved. After stirring for several hours, the ethanol was evaporated down and the resulting red oil was stirred with hexane–ether. The mixture was refrigerated for several days, during which a very small amount of precipitate formed. The hexane–ether supernatant was decanted off, and the remaining oil was dissolved with stirring in approximately 1 mL of ethanol. A yellow precipitate formed, which was filtered off to give a light-yellow powder, mp 94–96 °C.

1-(4-Cl,H). Benzal-4-chloroaniline (0.236 g) was added, with stirring, to a solution of 0.15 g (1 equiv) phenylnitromethane in 1 mL of diethyl ether. To this was added 5.7 μL (0.05 equiv) of diethylamine. The reaction mixture was stirred for several minutes till the Schiff base dissolved. The mixture was placed in a freezer overnight, during which a small amount of precipitate formed. The volume of solvent was reduced by one-half, a few drops of hexane were added, and the mixture stirred for an additional 1 h, after which the mixture was placed in a freezer for several days. A thick orange oil formed in addition to the white solid. The solid was filtered off, stirred vigorously in hexanes for 30 min, and then refiltered to yield 30 mg (7.8%) of off-white powder, mp 75–80 °C dec.

1-(4-Me,4-Br). An amount of 0.300 g of (4-bromophenyl)-nitromethane was added to a solution of 0.400 g (1.5 equiv) of benzal-*p*-toluidine in 1.5 mL of absolute ethanol. After the reactants had dissolved, 7.2 μL (0.05 equiv) of diethylamine was added, whereupon the solution turned yellow. The mixture was stirred for 2 min and then cooled in dry ice–acetone until a solid appeared. A few drops of hexanes were added, the mixture was stirred and then placed in a freezer for 5 days. The resulting precipitate was filtered off, stirred in hexanes for several minutes, and then refiltered to yield 0.237 g (41%) of bright yellow crystals, mp 95–97 °C dec.

1-(H,4-Br). To a solution of 0.300 g of (4-bromophenyl)-nitromethane in 1.5 mL of absolute ethanol was added 0.252 g (1 equiv) of benzalaniline. After the Schiff base had dissolved, 7.0 μL (0.05 equiv) of diethylamine was added with stirring. After stirring for 15 min at room temperature, the reaction mixture was cooled in an ice–rock salt bath, resulting in formation of a fine white precipitate. The mixture was stored in a freezer overnight, after which the mixture had almost completely solidified. The product was filtered off, stirred in approximately 2 mL of hexanes for 10 min, and refiltered to afford 0.450 g (82%) of a white powder that melted over a broad range above ~60°.

1-(4-Cl,4-Br). Preparation 1. To a solution of 0.300 g of (4-bromophenyl)nitromethane in 1.5 mL of absolute ethanol was added 0.301 g (1 equiv) of benzal-4-chloroaniline. After the Schiff base had dissolved, 7.2 μL (0.05 equiv) of diethylamine was added and the solution stirred for 15 min at room temperature. The reaction mixture was then cooled in dry ice–acetone till the solution became very viscous, and 1–2 mL of hexanes was added to form a precipitate. The mixture was placed in a freezer for 2 days, after which the product was filtered off, stirred in 1 mL of hexanes for several minutes, and refiltered to afford 0.124 g (21%) of pale yellow powder. Preparation 2. To a solution of 0.300 g of (4-bromophenyl)-nitromethane in 1.5 mL of absolute ethanol was added 0.301 g (1 equiv) of benzal-4-chloroaniline. After the Schiff base had dissolved, 7.2 μL (0.05 equiv) of diethylamine was added with stirring. After stirring for 15 min at room temperature, the

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reaction mixture was placed in a freezer for 2 days. The solvent was then evaporated to approximately one-fourth its original volume. An equal volume of hexanes was then added, and the stirring mixture was seeded with a few grains of the product from preparation 1. After stirring for another 15 min, the mixture was placed in a freezer overnight, during which the reaction mixture almost completely solidified. The product was filtered off, stirred in approximately 2 mL of hexanes for 30 min, and refiltered to afford 0.370 g (62%) of pale yellow powder, mp 83–85 °C.

1-(3-NO_2,4-Br). To a hot solution of 0.209 g of benzal-3-nitroaniline in 1 mL of ethanol was added 0.200 g (1 equiv) of (4-bromophenyl)nitromethane. The reaction mixture was stirred till the (4-bromophenyl)nitromethane dissolved and then allowed to cool to near room temperature. Diethylamine (4.8 μL, 0.05 equiv) was added and the solution stirred for 10 min. Cooling with dry ice–acetone failed to induce discernible precipitation, so the mixture was allowed to stir at room temperature. Within a short time a yellow precipitate began to appear and the mixture soon solidified. The product was filtered off, stirred in approximately 2 mL of hexanes for 15 min, and refiltered to afford 0.350 g (85%) of a bright yellow powder that melted over a very broad range above 78 °C.

1-(H,4-NO_2). Benzalaniline (0.249 g) was added to a stirring suspension of (4-nitrophenyl)nitromethane (0.250 g, 1 equiv) in 1 mL of absolute ethanol. Upon addition of 7.1 μL of diethylamine, the solution turned yellow. Over the next 2 h the (4-nitrophenyl)nitromethane dissolved with concomitant formation of a yellow precipitate. One milliliter of hexane was added and the mixture was placed in a freezer overnight. The product was filtered off, stirred in approximately 2 mL of hexanes for 15 min, and refiltered to give 0.38 g (76%) of bright yellow powder, mp 88–91 °C.

1-(4-Cl,4-NO_2). Benzal-4-chloroaniline (0.240 g) was added to a stirring suspension of (4-nitrophenyl)nitromethane (0.20 g, 1 equiv) in 1 mL of absolute ethanol. Within 30 s of adding 5.7 μL of diethylamine, the solution turned orange and the (4-nitrophenyl)nitromethane was dissolved with concomitant formation of a yellow precipitate. Within a minute, the mixture was too thick to stir, upon which 1 mL of hexanes was added and the mixture placed in a freezer. After 2 h the product was filtered off, stirred in approximately 2 mL of hexanes for 10 min, and refiltered to give 0.369 g (84%) of bright yellow powder, mp 115–117 °C.

1-(3-NO_2,4-NO_2). To a hot solution of 0.245 g of benzal-3-nitroaniline in 1 mL of ethanol was added 0.200 g (1 equiv) of (4-nitrophenyl)nitromethane. The mixture was heated and stirred till the Schiff base was completely dissolved and then allowed to cool to near room temperature. Diethylamine (5.7 μL, 0.05 equiv) was added and the solution stirred until the (4-nitrophenyl)nitromethane dissolved. The mixture was stirred for another 30 min at room temperature, during which a large amount of yellow precipitate formed. The mixture was placed in a freezer for 2 h. The product was then filtered off, stirred in approximately 2 mL of hexanes for several minutes, and refiltered to give 0.333 g (74%) of bright yellow powder, mp 127–130 °C dec.

Spectra. UV-visible spectra were obtained with a Perkin-Elmer Model 559A spectrometer. Proton NMR spectra were obtained at 300 MHz with a General Electric widebore GN-300 instrument. All NMR spectra were obtained at ambient temperature.

Kinetics. All experiments were carried out in 50% Me_2SO–50% water maintained at 0.5 M ionic strength with KCl. Reactions were run in a Perkin-Elmer 559A spectrometer equipped with a thermostated five-cell changer at 5 °C. To prevent fogging of the cells, the cells were treated with an antifog solution, and the sample compartment was purged with dry nitrogen throughout the run. The reactions were monitored at 280 nm for Y = H, 284 nm for Y = 4-Br, and 340 nm for Y = 4-NO_2; these wavelengths are at or near the absorbance maxima of the corresponding nitronic acids.

Data from slow reactions employing the five-cell changer were collected with a computerized data acquisition system. For fast reactions where only a single cell could be monitored, the absorbance versus time data was extracted from the chart recorder. Rate constants were evaluated from the absorbance versus time data as described in ref 16 by means of a personal computer graphics package (Cricket Graph).

To conduct the carbanion expulsion reactions, a preweighed sample of 1–3 mg of the adduct was dissolved in 0.2 mL of dry acetonitrile. Approximately 3–10 μL of this solution (enough to produce a large absorbance change) was added to a cuvette containing approximately 2 mL of the appropriate buffer solution equilibrated to the proper temperature in the sample compartment. The solution was immediately stirred with a Teflon stirring rod.

To obtain values of k_{taut} for the conversion of the nitronic acids to phenylnitromethanes, a 1.0×10^{-3} M solution of the phenylnitromethane anion was prepared by adding 10 μL of a 0.10 M solution of the phenylnitromethane in Me_2SO to 1 mL of 1.0×10^{-3} M KOH. The reaction was initiated by adding 100 μL of this solution to approximately 2 mL of the appropriate acidic buffer, resulting in formation of the nitronic acid.

Determination of the pK_a of 3-Nitroaniline. The pK_a was determined in 50% Me_2SO–50% water at 20 °C, μ = 0.5 M (KCl) by a classical spectrophotometric procedure, exploiting the fact that the basic form absorbs at 380 nm ($\epsilon \approx 1300$ M^{-1} cm^{-1}) while the protonated form does not absorb at this wavelength. Solutions of 5×10^{-4} M 3-nitroaniline were prepared containing 1.0, 0.10, 0.05, and 0.010 M HCl and 0.001 M KOH. These gave absorbances of 0.0, 0.140, 0.234, 0.474, and 0.638, respectively. Plotting this data according to eq 17, using the value of the absorbance in the KOH solution as A_0,

$$\frac{A_0}{A} = 1 + \frac{a_{H^+}}{K_a^{BH}} \qquad (17)$$

gave an intercept of unity and slope = $1/K_a^{BH}$ = 35.7. Hence K_a^{BH} = 0.0280, corresponding to a pK_a^{BH} = 1.55.

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