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Imine-Forming Elimination Reactions. 2. Imbalance of Charge Distribution in the Transition State for Carbinolamine Dehydration[1]

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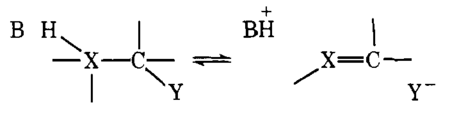
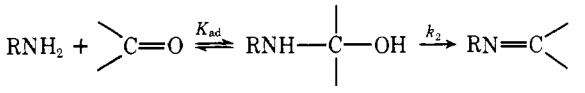
Abstract: The rate constants for hydroxide ion catalyzed dehydration of the carbinolamine intermediate in acethydrazone formation from substituted benzaldehydes are slightly increased by electron-donating benzaldehyde substituents: $\rho^+ = -0.5$ for the reactions of *p*-methoxy-, *p*-chloro-, and *p*-nitrobenzaldehydes. Hydroxide ion catalyzed expulsion of the alcohol from carbinolamine ethers, *p*-$CH_3PhSO_2NHNHCH(OR)Ph$-*p*-Cl, is greatly accelerated by electron-withdrawing substituents in the alcohol moiety, ROH: $\beta_{lg} = -1.05$. These observations and the previously reported large effect of electron-withdrawing substituents on nitrogen ($\beta_N = -1.0$) suggest an imbalanced transition state involving extensive N-H and C-O bond breaking with relatively little development of C-N double bond character. The data suggest that in spite of the value of $\beta_{lg} = -1.05$, C-O cleavage is not complete; the large substituent effect may be accounted for by an imbalance between the amounts of C-O cleavage and developing solvation of the departing oxyanion in the transition state. Bronsted α values for general acid catalysis of the elimination of ROH from *p*-$CH_3PhSO_2NHNHCH(OR)Ph$-*p*-Cl are 0.69, 0.60, and 0.44 for R = CH_3CH_2-, $ClCH_2CH_2$-, and CF_3CH_2-, respectively. The results add both the acid- and base-catalyzed eliminations to the small group of reactions for which there is strong evidence supporting a concerted mechanism of catalysis.

We have been interested in mapping the "electronic anatomy" of the transition state for base-catalyzed carbinolamine dehydration (eq 1, X = N, Y = OH^-) by determining the effects on the rate of polar substituents attached to the different reacting atoms.[3,4] This reaction is the same as elimination reactions from carbon to form olefins[5] (eq 1, X = C) except



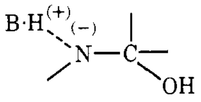
$$\mathrm{B} + \mathrm{H{-}X{-}C{-}Y} \rightleftharpoons \overset{+}{\mathrm{BH}} + \mathrm{X{=}C} + \mathrm{Y^-} \qquad (1)$$



$$\mathrm{RNH_2} + \mathrm{{>}C{=}O} \overset{K_{ad}}{\rightleftharpoons} \mathrm{RNH{-}\overset{|}{\underset{|}{C}}{-}OH} \xrightarrow{k_2} \mathrm{RN{=}C{<}} \qquad (2)$$

for the substitution of the more electronegative nitrogen atom for carbon and the presence of a free electron pair on the nitrogen atom that may facilitate leaving group expulsion. The loss of hydroxide ion brings about a change in the pK_a of the NH group from approximately 27 to 0, and it is this large change in acidity that provides the driving force for general base catalysis.[4] Carbinolamine dehydration is the second step of imine formation from carbonyl compounds and amines (eq 2) and is usually rate determining above neutral pH.[4,6]

We have reported previously that the Bronsted slope of β = 0.7 for general base catalysis and a large increase in rate with electron-withdrawing substituents on nitrogen ($\beta_N = -1.0$) imply that there is a large amount of proton abstraction in the transition state for carbinolamine dehydration, with little movement of the developing negative charge away from the nitrogen atom into the incipient double bond.[3,4] We therefore expected that this negative charge would be stabilized by electron-withdrawing substituents on the central carbon atom and that there would be little expulsion of the leaving OH^- group in the transition state (**1**); i.e., that the reaction would



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be similar to E1cB-like elimination reactions of carbon compounds. The experiments described here show that, in fact, the transition state is stabilized by electron-*donating* substituents on carbon and that the rate of expulsion of a series of leaving alkoxide groups is markedly increased by electron-withdrawing substituents. These results indicate that there has been a considerable amount of C-O cleavage as well as proton transfer in the transition state, but that this is accompanied by little or no double bond formation between carbon and nitrogen. It appears that double bond formation and change of the carbon and nitrogen atoms from sp^3 to sp^2 hybridization lag behind other processes in the transition state. This is a striking example of the imbalance of the extent to which different processes may proceed in the transition state. The best known previous example is the ionization of nitroalkanes, in which rehybridization of a single reacting carbon atom appears to lag behind proton removal and electron delocalization into the nitro substituent in the transition state.[7]

We also report that the rate of general acid catalyzed expulsion of -OR from carbinolamine ethers is increased by electron-withdrawing substituents in the leaving group with weak acid catalysts but shows a decrease and then a reversal of this substituent effect as the strength of the catalyzing acid is increased, and that the Bronsted α value shows a corresponding increase as the pK of the leaving alcohol increases. These results provide further evidence for a concerted mechanism of general acid catalysis of leaving group expulsion in these reactions.

Experimental Section

Materials. Reagent grade inorganic salts and formic and acetic acids were used without further purification. Other organic reagents were recrystallized, distilled, or sublimed before use. Acetonitrile was dried by distillation from phosphorus pentoxide or calcium hydride. Acethydrazide, which is hygroscopic, was usually stored and weighed under dry nitrogen or argon. *p*-Methoxybenzaldehyde was washed with 0.5 M sodium bicarbonate solution and then with water and dried over magnesium sulfate prior to distillation under reduced pressure, and the purified aldehyde was stored under argon. Glass distilled water was used in all experiments. Concentrated stock solutions of aldehydes in absolute ethanol, freshly prepared each week, were stored cold under argon and were diluted with water before addition to reaction mixtures. The final concentration of ethanol in the reaction mixtures containing substituted benzaldehydes was less than 0.7%. In the kinetic studies of acethydrazone formation the reaction mixtures contained approximately 10^{-4} M disodium EDTA.

α,α-Dibromo-*p*-chlorotoluene was prepared by the photoaddition of bromine[8] (1 mol) in 400 ml of carbon tetrachloride to 0.25 mol of *p*-chlorotoluene in 380 ml of carbon tetrachloride. The fraction of product boiling at 100-105 °C (1.2 mm) was collected under nitrogen in a yield of 60 g (84%).

Trifluoroethyl Acetal of *p*-Chlorobenzaldehyde. To 150 ml of dry 2,2,2-trifluoroethanol was added carefully 8 g of "50% oil suspension" of sodium hydride (Alfa Inorganics) which had been resuspended in petroleum ether. The mixture was cooled in an ice bath and kept under nitrogen during the addition. To the resulting solution of sodium 2,2,2-trifluoroethoxide was added 28.4 g (0.1 mol) of α,α-dibromo-*p*-chlorotoluene, and the mixture was refluxed gently for 2 h. The mixture was cooled, and the insoluble sodium bromide was removed by filtration and washed with ether. The filtrate was diluted with ether and washed twice with sodium chloride solution, twice with 2 M sodium bisulfite and twice again with sodium chloride solution, and dried with potassium carbonate. After evaporation of the ether the residue was distilled and 22.7 g of the fraction boiling at 69-69.5 °C (0.55 mm) was collected.

Anal.[9a] Calcd for $C_{11}H_9ClF_6O_2$: C, 40.95; H, 2.94; Cl, 10.99. Found: C, 40.80; H, 2.83; Cl, 11.33.

2-Chloroethyl acetal of *p*-chlorobenzaldehyde was prepared by refluxing *p*-chlorobenzaldehyde (0.25 mol) with 1.0 mol of 2-chloroethanol in 300 ml of benzene containing 1.5 g of *p*-toluenesulfonic acid for several days in an apparatus equipped with a Dean-Stark trap, until a total of 4.8 ml of water had been collected. The benzene solution was washed with 1 M sodium bicarbonate solution and then with water and was dried over potassium carbonate. After evaporation of the solvent, most of the aldehyde impurity was removed from the residue by vacuum sublimation, and the remaining liquid was distilled under reduced pressure. A small fore-run was discarded, and two fractions, bp 99-105 °C (0.07 mm) and 112-115 °C (0.05-0.07 mm) were collected. NMR spectra for the two fractions were identical except for the presence of a trace contaminant, δ 1.26 ppm, in the lower boiling fraction. The total yield was 37 g (56%). Analysis of the higher boiling fraction gave: Anal.[9a] Calcd for $C_{11}H_{13}Cl_3O_2$: C, 46.60; H, 4.62; Cl, 37.52. Found: C, 46.60; H, 4.69, Cl, 37.30.

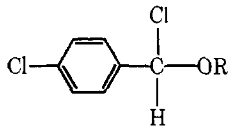
Diethyl acetal of *p*-chlorobenzaldehyde was prepared by the reaction of 0.1 mol of *p*-chlorobenzaldehyde with 100 ml of ethanol at room temperature in the presence of 0.5 g of *p*-toluenesulfonic acid and 20 g of sodium sulfate. After 2 days the acid was neutralized with 10 M potassium hydroxide, and the solution was filtered and concentrated. The residue was diluted with ether, washed once with water, and dried over potassium carbonate. After solvent evaporation the residue was distilled, and the fraction boiling at 65-72 °C (0.2 mm) [lit.[9b] bp 108 °C (3 mm)] was collected; yield, 8.7 g (40%).

Preparation of α-Chloro Ethers. *p*-α-Dichlorobenzyl alkyl ethers, ClPhCH(Cl)(OR), were prepared from the corresponding acetals of *p*-chlorobenzaldehyde and freshly distilled acetyl chloride by modifications of the method of Straus and Heinze.[10] An initial ratio of 1.6 ml of acetyl chloride and 20 μl of thionyl chloride to 10 mmol of acetal was used; additional acetyl chloride and thionyl chloride were sometimes added during the course of the reaction to replace losses from evaporation during prolonged reaction times. The progress of the reaction was most conveniently followed by withdrawal of a sample of the reaction mixture, dilution with carbon tetrachloride and measurement of the NMR spectrum: during the course of the reaction the resonance corresponding to the α proton of the acetal at $\delta \simeq 5.4$ ppm is replaced by that for the corresponding proton in the α-chloro ether at $\delta \simeq 6.4$-6.6 ppm. For the trifluoroethyl ether the progress of the reaction was followed by hydrolysis of a 5 μl sample of the reaction mixture in 1:1 acetonitrile-0.20 M aqueous potassium hydroxide solution, and assay of the resulting aldehyde by measurement of the absorbance at 285 nm of its semicarbazone formed in 0.1 M semicarbazide buffer, 50% hydrochloride.

After formation of the α-chloro ethers was complete, acetyl chloride, thionyl chloride, and the ester product of the reaction were removed under vacuum from the reaction flask without transferring the reaction mixture, and the residue was distilled under vacuum. The lower boiling fraction, which ordinarily was contaminated with aldehyde, was discarded, and the product from the higher boiling fraction(s) was further purified if necessary by redistillation. The identity and purity of the α-chloro ethers was determined by NMR spectrometry and by determination of (a) the amount of HCl liberated by reaction of a weighed sample with 1.3 ml of 0.23 N KOH in 77% ethanol, measured by titration of the base remaining after the reaction, and (b) the amount of *p*-chlorobenzaldehyde formed by hydrolysis in a 50% acetonitrile/water solution, 0.1 N in KOH, measured spectroscopically as the semicarbazone at 285 nm. The ethers did not give satisfactory elemental analyses, presumably as a result of partial hydrolysis. Reaction conditions for the preparation of the α-chloro ethers, and properties of the products, are given in Table I.

Solutions of α-tosylhydrazino ethers were prepared on the day of use in 0.5 ml of dry acetonitrile from the appropriate α-chloro ethers (0.03 mmol) and 0.06-0.09 mmol of *p*-toluenesulfonylhydrazide. Ordinarily 2,6-lutidine (0.045-0.09 mmol) was used to trap the acid liberated in the reaction; silver oxide was used on some occasions with the trifluoroethyl derivative, and for these reactions the cold reaction mixture was diluted tenfold with acetonitrile and centrifuged, and the precipitate was discarded, before the solution was used. Reaction conditions for formation of the α-tosylhydrazino ethers were as follows: 2,2,2-trifluoroethyl: 5-15 min at room temperature in the presence of 2,6-lutidine, or approximately 2 min at approximately −40 °C in the presence of silver oxide; 2-chloroethyl: 5-10 min at 0 °C in the presence of 2,6-lutidine; ethyl: 5-10 min at approximately −40 °C in the presence of 2,6-lutidine. After formation of the α-tosylhydrazino ethers, the solutions were diluted with acetonitrile and kept

Table I. Preparation and Properties of *p*,α-Dichlorobenzyl Alkyl Ethers



−OR	Reaction conditions	Bp, °C	Product		
			Mol HCl/Mol[a]	Mol PCBA/Mol[a]	NMR, δ
$-OCH_2CF_3$	3.5 h reflux, 15 h room temp, 2 h additional reflux	53–56.5 (0.2 mm)	0.85	0.78	4.10 (2), 6.57 (0.7), 7.45 (3.7)[b]
$-OCH_2CH_2Cl$	36 h reflux, 2 days room temp, 24 h additional reflux	95–96 (0.12 mm)	1.00	1.00	3.56–4.52 (4), 6.48 (1), 7.38 (4.1)
$-OCH_2CH_3$	2 h reflux, ~16 h room temp, 6 h additional reflux	70–74 (0.3–0.4 mm)	1.03	0.98	1.35 (3), 3.82 (1.9), 6.39 (0.9), 7.28 (3.9)

[a] Assay of a representative sample (see text). [b] Minor peaks at δ 5.87 and 10.0 due to acetal and aldehyde, respectively, were observed in this product.

Table II. Experimental Conditions for Reactions of Acethydrazide, $CH_3C(O)NHNH_2$, with Substituted Benzaldehydes

Substituent	pH range	Type expt	$[CH_3C(O)NHNH_2]$, M	ArCHO, M	λ, nm
p-OCH_3	11.8-12.7	Pseudo-first-order	0.03	3×10^{-5}	310
	8.0-10.6	Initial rate	0.1	1.5×10^{-3}	325
p-NO_2	*a*	Pseudo-first-order	0.005-0.02	5×10^{-5}	310, 320

[a] $C_{OH^-} = 0.005$-0.050 M.

at or below −40 °C. The ethyl and 2-chloroethyl compounds (0.1 ml) were further diluted immediately before use with 0.4 ml of 50% aqueous acetonitrile.

Equilibrium Constants. The equilibrium constant for carbinolamine formation from *p*-methoxybenzaldehyde and acethydrazide was determined in triethylenediamine buffer, 0.05 M, pH 9.3, from the change in absorbance at 285 nm, ΔA, extrapolated to time zero, upon addition of a solution of *p*-methoxybenzaldehyde of known absorbance to buffer solutions containing known concentrations of acethydrazide. Triplicate determinations were made at each of five acethydrazide concentrations between 1.9 and 5.5 M. The absorbance change expected for complete conversion of the aldehyde to a tetrahedral adduct was greater than 96% of the absorbance of the free aldehyde, as estimated from the decrease in absorbance upon addition of the aldehyde to 0.2 M sulfite buffer solution, 85% dianion. The equilibrium constant K_{ad} for carbinolamine formation from acethydrazide was determined from the relationship $K_{ad} = \alpha/\{(1-\alpha)[CH_3C(O)NHNH_2]\}$, in which α is the fraction of aldehyde converted to carbinolamine, and from the negative abscissa intercept of double reciprocal plots of ΔA against acethydrazide concentration.

The equilibrium constant for carbinolamine formation from *p*-nitrobenzaldehyde and acethydrazide was determined kinetically[4] in 0.1 M 3-quinuclidinol buffer, 80% base, pH 10.75, from the dependence of the pseudo-first-order rate constants for acethydrazone formation, k_ψ, on the concentration of acethydrazide at concentrations between 0.04 and 0.22 M. The equilibrium constant for carbinolamine formation from unhydrated plus hydrated *p*-nitrobenzaldehyde was obtained from the negative abscissa intercept of a double reciprocal plot of k_ψ against acethydrazide concentration. A correction[11] of 20% was applied to give K_{ad} for the unhydrated aldehyde.

An equilibrium constant of 14 M^{-1} for addition of hydroxide ion to hydrated plus unhydrated *p*-nitrobenzaldehyde was determined at 25 °C and ionic strength 1.0 (KCl) from the change in absorbance at 268 nm upon addition of *p*-nitrobenzaldehyde to solutions containing between 0.01 and 1.0 M potassium hydroxide. This value is in satisfactory agreement with the value of 13.3 M^{-1} measured by Greenzaid[12] at varying ionic strength and the thermodynamic value of 16.2 M^{-1} determined by Bover and Zuman.[13]

Kinetics. The reaction of acethydrazide with para-substituted benzaldehydes was studied at 24.6 ± 0.5 °C and ionic strength 1.0 (potassium chloride) using methods previously described.[3,4] Experimental conditions for these studies are summarized in Table II. For the initial rate experiments using *p*-methoxybenzaldehyde, the absorbance at time infinity was determined by dilution of a solution of the product formed in the presence of 0.12 M acethydrazide and 0.05 M potassium hydroxide.

Observed pseudo-first-order rate constants, k_{obsd}, for acethydrazone formation from *p*-nitrobenzaldehyde at high concentrations of base were corrected for equilibrium formation of the neutral and anionic hydrate of *p*-nitrobenzaldehyde and for equilibrium formation of the carbinolamine (K_{ad}) according to

$$k_{cor} = k_{obsd}(1 + K_{ad}[N]\alpha)/K_{ad}[N]\alpha \qquad (3)$$

where [N] is the concentration of acethydrazide and α is the fraction of aldehyde in the unhydrated form. The value of α is given by

$$\alpha = 1 - \left(\frac{K_2[OH^-] + K_1}{1 + K_1 + K_2[OH^-]}\right) \qquad (4)$$

where $K_1 \simeq 0.25$ and $K_2 = 17.5$ M^{-1} are the equilibrium constants for addition of water[11] and hydroxide ion, respectively, to the unhydrated aldehyde. Values of the second-order rate constant calculated with and without correction for equilibrium formation of the anionic hydrate of the aldehyde at high pH are illustrated in Figure 1.

The formation of the tosylhydrazone of *p*-chlorobenzaldehyde from α-tosylhydrazino ethers was followed spectrophotometrically at 290 or 300 nm, after introduction of a 30–100 μl sample of the carbinolamine ether in acetonitrile or acetonitrile-water into 2.9–3.0 ml of aqueous buffer solution, ionic strength 1.0 (tetramethylammonium chloride) at 25 °C. A Gilford Model 2000 or a Zeiss PMQII spectrophotometer equipped with a Beckman recorder was used. For fast reactions, 0.10 ml of an acetonitrile solution of the carbinolamine ether was added to 2.4 ml of aqueous buffer solution using the rapid mixing device of Perlmutter-Hayman and Wolff,[14] as described by Gravitz and Jencks.[15a]

Product Identification. The products of the reaction of α-tosylhydrazino ethers in 0.02 M acetate buffer, 50% acid, were determined

Table III. Rate and Equilibrium Constants for Base-Catalyzed Formation of Acethydrazones from Para-Substituted Benzaldehydes, X-C_6H_4CHO[a]

X	$-OCH_3$	-Cl	$-NO_2$
K_{ad}, M^{-1}	0.05	0.7^b	10.8
$k_2^{OH\,c}$, $M^{-1}\,s^{-1}$	40	14^b	7.0
$k_2^{QDL\,d}$, $M^{-1}\,s^{-1}$	$2.6 \times 10^{-2\,e}$	$8.8 \times 10^{-3\,b}$	
$k_2^{TED\,d}$, $M^{-1}\,s^{-1}$	$6.8 \times 10^{-3\,e}$	$2.3 \times 10^{-3\,b}$	

[a] At 25 °C, ionic strength 1.0 (KCl). Rate constants are defined for the processes of eq 2. [b] Reference 4. [c] Based on hydroxide ion concentration. [d] Rate constants for catalysis by the conjugate bases of 3-quinuclidinol (QDL), pK_a' 10.13, and triethylenediamine (TED), pK_a' 9.22. [e] Determined from the intercept at 100% free base of plots of the apparent catalytic constant for total buffer against buffer composition at three or more buffer ratios.

after acidification of the reaction mixtures with 0.10 ml of 1 M hydrochloric acid and extraction of the products into ether. The α-tosylhydrazino ethers used in these experiments were prepared in 1 ml of dry acetonitrile from 0.18 mmol of *p*-toluenesulfonylhydrazide and 0.10-0.13 mmol of α-chloro ether in the presence of 0.17 mmol of 2,6-lutidine, under conditions similar to those used for production of these compounds for kinetic studies. These solutions were diluted twofold with acetonitrile and then fivefold with 50% acetonitrile/water before addition of 0.1 to 5 ml of aqueous buffer solution. The absorption maxima in ether for the products extracted from the buffer appeared at 281 nm, identical with λ_{max} in ether for the authentic tosylhydrazone. A small shoulder was observed at 260 nm, presumably corresponding to some *p*-chlorobenzaldehyde formed from the α-chloro ethers and traces of water under the conditions for generating the α-tosylhydrazino ethers. Recovery of the tosylhydrazone was calculated from the absorbance of the products at 300 nm, where the absorbance of the aldehyde is negligible, and corresponded to 53-59% of the theoretical yield of tosylhydrazone from α-chloro ether. If the formation of aldehyde, estimated from the absorbance of the products at 253 nm, and corrected for the absorption of the tosylhydrazone at this wavelength, was taken into account, the recovery of aldehyde plus tosylhydrazone from the α-chloro ethers was 68-73%.

Results

Equilibrium Constants for Carbinolamine Formation. The equilibrium constants, K_{ad}, for carbinolamine formation from acethydrazide and benzaldehydes increase with electron-withdrawing substituents on the aldehyde (Table III). The results are consistent with a ρ^+ value of ~1.5, which may be compared with ρ^+ values of ~1.3 and 1.81 for the addition of methoxyamine[16] and semicarbazide,[17] respectively, and with ρ values of 1.4 and 2.0 (in methanol) for the addition of water[12,13] and methanol,[18] respectively.

Base Catalysis of Acethydrazone Formation from Substituted Benzaldehydes. At pH values between 9 and 13, acethydrazone formation from *p*-methoxybenzaldehyde is subject to catalysis by hydroxide ion, and exhibits a pH-rate profile analogous to that for the previously described reaction of *p*-chlorobenzaldehyde.[4] The reaction of *p*-nitrobenzaldehyde with acethydrazide is also catalyzed by hydroxide ion. At high pH values the apparent rate constants for this catalysis level off, as a result of formation of the anionic hydrate of *p*-nitrobenzaldehyde; corrections for formation of the neutral and anionic hydrate of this aldehyde were made as described in the Experimental Section. At alkaline pH values the rate-determining step for these reactions is the dehydration of the carbinolamine intermediate (eq 2). This was shown for *p*-methoxybenzaldehyde at pH 9.3 in the presence of 2-6 M acethydrazide by the observation of a rapid initial drop in the absorbance of the aldehyde at 285 nm, followed by a much slower absorbance change due to product formation. The pseudo-first-order rate constants for acethydrazone formation from *p*-nitrobenzaldehyde at pH 10.75 level off with increasing concentration of acethydrazide (0.04-0.2 M) as a result of accumulation of the intermediate.

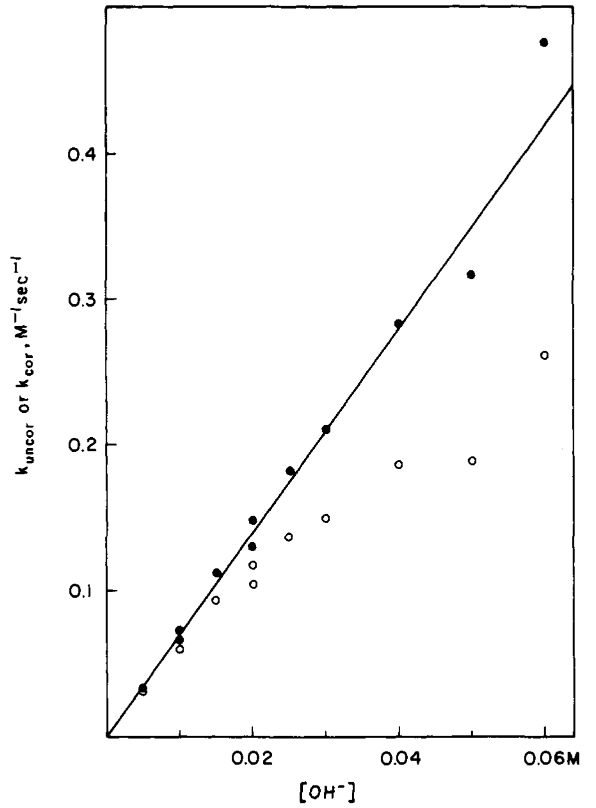


Figure 1. Second-order rate constants for acethydrazone formation from *p*-nitrobenzaldehyde in potassium hydroxide solution without (○) and with (●) correction for formation of the anionic hydrate. Values of k_{uncor} were calculated from the relationship $k_{uncor} = k_{obsd}\,(1 + K_1[N] + K_{ad}[N])/K_{ad}[N]$, where k_{obsd} is the observed pseudo-first-order rate constant, using values of K_1 and K_{ad} of 0.25 and 10.8 M^{-1}, respectively. The corrected values were calculated from eq 3 and 4 using K_2 = 17.5 M^{-1}. The corrected line corresponds to a third-order catalytic constant for hydroxide ion of 7.0 $M^{-2}\,s^{-1}$.

The base-catalyzed reaction follows the rate law $v = k_3[RNH_2][{>}C{=}O][B]$, in which the apparent third-order rate constant k_3 includes the equilibrium constant for carbinolamine formation and the rate constant for carbinolamine dehydration (eq 2). The values of k_3 for hydroxide ion catalyzed acethydrazone formation, measured at low concentrations of acethydrazide, were found to be 2.0, 9.8, and 730 $M^{-2}\,s^{-1}$ for *p*-methoxy-, *p*-chloro-, and (unhydrated) *p*-nitrobenzaldehyde, respectively. This acceleration by electron-withdrawing substituents is the result of a large increase in K_{ad} that is partly compensated by a smaller and opposite substituent effect on k_2^{OH}. Values of the second-order rate constants for hydroxide ion catalysis of carbinolamine dehydration, k_2^{OH}, were calculated from the relationship $k_3 = K_{ad}k_2^{OH}$ and are given in Table III.

Formation of acethydrazones from substituted benzaldehydes is also catalyzed by buffers. For *p*-methoxybenzaldehyde this catalysis was found to be proportional to both the acidic and the basic components of the buffer; catalytic constants for dehydration of the carbinolamine by the basic component of the buffer (Table III) were determined from the intercepts at 100% base of plots of k_{app} for total buffer against the fraction of base in the buffers. The ratios of the catalytic constants for the reactions of *p*-methoxy- and *p*-chlorobenzaldehydes are 2.8, 3.0, and 2.8 for catalysis by hydroxide ion, 3-quinuclidinol, and triethylenediamine, respectively. Thus, the results provide no evidence for a change in the Bronsted coefficient with changing substituent on the aldehyde.

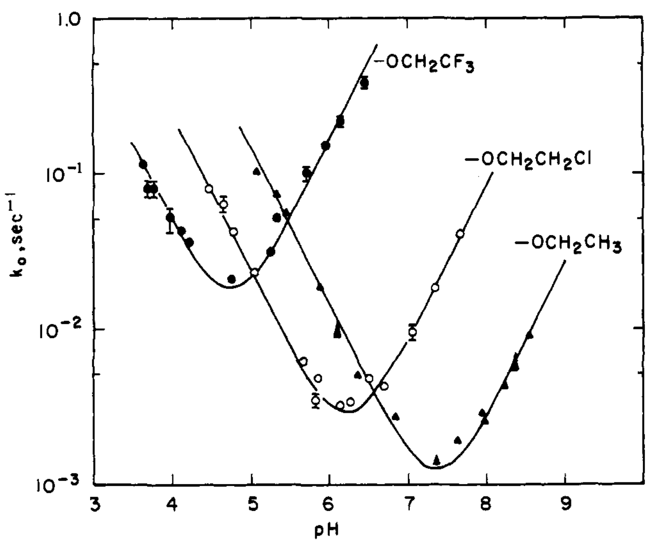
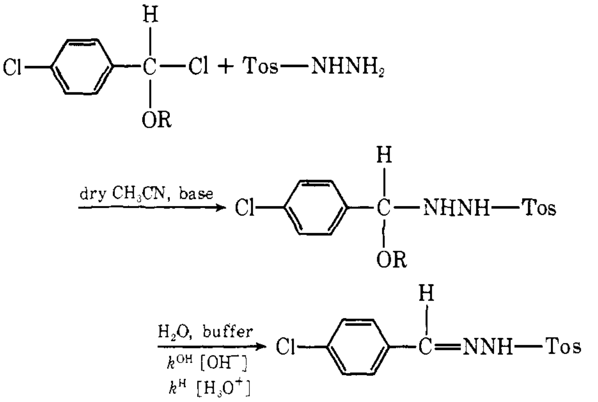


Figure 2. Dependence on pH of the first-order rate constants, k_0, extrapolated to zero buffer concentration, for elimination of alcohols from α-tosylhydrazino-*p*-chlorobenzyl alkyl ethers, *p*-$CH_3C_6H_4SO_2NHNHCH(OR)C_6H_4$-*p*-Cl, at 25 °C and ionic strength 1.0 [$(CH_3)_4NCl$]. The lines are theoretical curves based on the rate constants given in Table IV.

Decomposition of Carbinolamine Ethers in Aqueous Solution. The reaction of *p*,α-dichlorobenzyl alkyl ethers (1-[1-chloro-1-alkoxymethyl]-4-chlorobenzenes) with *p*-toluenesulfonylhydrazide in dry acetonitrile gave products which on addition to aqueous buffers exhibited a time-dependent absorbance change that was followed at 290-300 nm. The product, *p*-chlorobenzaldehyde tosylhydrazone, was identified by its ultraviolet spectrum after acidification of the aqueous buffer and extraction with ether. This sequence of reactions is shown in eq 5.



(5)

The product tosylhydrazone was not recovered quantitatively, partly as a result of formation of *p*-chlorobenzaldehyde as a side product. The most likely source of this aldehyde side product is hydrolysis of the α-chloro ethers by traces of water in the reaction mixture used for the generation of the α-tosylhydrazino ethers or hydrolysis of unreacted α-chloro ether after addition of the acetonitrile solution to the aqueous buffer. In 0.05 M cacodylate buffer, pH 5.9 and 6.3, hydrolysis of α,*p*-dichlorobenzyl trifluoroethyl ether, which is expected to be the least reactive of the ethers used, was shown to occur at a rate sufficiently fast that it did not interfere with the measurement of the rate for tosylhydrazone formation. Furthermore, the extinction coefficient of *p*-chlorobenzaldehyde is only 15 and 4% of that of the tosylhydrazone at 290 and 300 nm, respectively, so that the presence of small amounts of unreacted α-chloro ether which hydrolyze concomitantly with the breakdown of the α-tosylhydrazino ethers should have a negligible effect on the observed kinetics.

Table IV. Buffer-Independent Rate Constants for Tosylhydrazone Formation from α-Tosylhydrazino-*p*-chlorobenzyl Alkyl Ethers, *p*-$CH_3C_6H_4SO_2NHNHCH(OR)C_6H_4$-*p*-Cl[a]

R	pK_{ROH}[b]	k^{OH},[c] M^{-1} s^{-1}	k^{H},[d] M^{-1} s^{-1}
CF_3CH_2-	12.37	1.6×10^7	5.0×10^2
$ClCH_2CH_2$-	14.31	8.5×10^4	2.4×10^3
CH_3CH_2-	16	2.8×10^3	1.4×10^4

[a] At 25 °C, ionic strength 1.0 ($(CH_3)_4NCl$). [b] Reference 19. [c] In terms of antilog (pH −14). [d] In terms of antilog (−pH).

Pseudo-first-order rate constants, extrapolated to zero buffer concentration, for tosylhydrazone formation from α-tosylhydrazino ethers are shown in Figure 2. The reaction is catalyzed by both hydroxide and hydronium ions. As the pK_a of the leaving alcohol[19] is decreased, the rate constants (Table IV) for hydroxide ion catalysis increase steeply, whereas the rate constants for hydronium ion catalysis decrease somewhat less steeply, resulting in an increase in the rate constants observed at the minima of the pH-rate profiles and a shift in these minima to lower pH, with decreasing pK_a of the alcohol. The rate constant of 1.1×10^3 M^{-1} s^{-1} for hydroxide ion catalyzed dehydration of the corresponding carbinolamine[4] shows that hydroxide ion is a slightly less good leaving group than ethoxide ion; hydroxide ion behaves like the anion of an alcohol of p*K* 16.4. In the reactions of acetic acid with nucleophiles and the dehydration of bicarbonate ion, hydroxide ion also behaves like the anion of an alcohol of pK 16.4–16.5.[20]

Tosylhydrazone formation from carbinolamine ethers is subject to general acid catalysis by buffers. Catalytic constants for the dehydration of carbinolamine ethers by a series of carboxylic and cacodylic acids are given in Table V.

Discussion

Substituent Effects. We shall attempt to map out the charge distribution in the transition state for the base-catalyzed elimination of $^-$OR from ArCH(OR)NR′H by comparing substituent effects on the rate, i.e., transition-state stability, with effects on equilibria. For the proton transfer this comparison gives the Bronsted coefficient β, and analogous comparisons with the appropriate ionization constants, based on plots of log *k* against pK_a, give proportionality constants β_N and β_{lg} for the effects of polar substituents on the nitrogen atom and the leaving RO$^-$ group, respectively. The charge development on the central carbon atom is estimated from ρ. Some comment on these comparisons is in order in view of questions that have been raised recently regarding the interpretation of Bronsted coefficients.[7] Since polar substituents exert their effect through electrostatic interactions, the Bronsted coefficient is a measure of the relative amount of charge development that is "seen" by the substituent in the transition state and product. For a simple proton transfer that is unaccompanied by other processes, it is reasonable to suppose that this charge development increases monotonically as the proton transfer proceeds. For such reactions the Bronsted coefficient is a measure of the amount of proton transfer, and the amount of proton transfer may be defined in terms of the Bronsted coefficient. Other simple bond-forming and bond-breaking processes may be treated similarly. If several processes are occurring around the reacting atom, when a central atom reacts with both a leaving and an attacking group or charge is delocalized into a nitro group, for example,[7] the value of α or β is still a measure of the amount of charge development in the transition state, but may not be a monotonic function of the

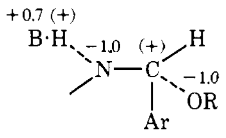
Table V. General Acid Catalysis of Tosylhydrazone Formation from α-Tosylhydrazino-p-chlorobenzyl Alkyl Ethers p-$CH_3C_6H_4SO_2NHNHCH(OR)C_6H_4$-$p$-Cl[a]

Catalyst	pK[b]	Concn, M	Fraction acid	k_{app},[c] $M^{-1}\,s^{-1}$	k^{HA}, $M^{-1}\,s^{-1}$
			R = CF_3CH_2-		
Chloroacetic acid (**1**)	2.74	0.10-0.40	0.05	0.43	
		0.10-0.40	0.09	0.53	
		0.10-0.40	0.10	0.71	8
Methoxyacetic acid (**2**)	3.52	0.04-0.20	0.20	0.64	
		0.08-0.40	0.40	0.96	2.8
Formic acid (**3**)	3.62	0.05-0.20	0.20	0.44	
		0.05-0.20	0.50	0.96	1.80
Acetic acid (**4**)	4.65	0.05-0.20	0.20	0.15	
		0.05-0.20	0.50	0.40	0.79
Cacodylic acid (**6**)	6.30	0.05-0.20	0.70	<0.17	
		0.05-0.20	0.90	0.16	0.18
			R = $ClCH_2CH_2$-		
Methoxyacetic acid (**2**)	3.52	0.08-0.40	0.06	0.104	
		0.08-0.40	0.10	0.23	2.0
Acetic acid (**4**)	4.65	0.08-0.40	0.05	0.024	
		0.08-0.40	0.30	0.086	
		0.08-0.40	0.50	0.12	0.30
Dimethylmalonic acid (**5**)	5.8	0.04-0.20	0.17	0.024	
		0.04-0.20	0.50	0.067	0.14
Cacodylic acid (**6**)	6.30	0.04-0.20	0.30	0.021	
		0.04-0.20	0.60	0.028	
		0.04-0.20	0.80	0.032	0.036
			R = CH_3CH_2-		
Acetic acid (**4**)	4.65	0.10-0.50	0.20	0.12	
		0.10-0.50	0.30	0.13[d]	
		0.10-0.50	0.50	0.18[d]	0.45
Dimethylmalonic acid (**5**)	5.8	0.04-0.20	0.20	0.040	
		0.05-0.25	0.40	0.092	0.22
Cacodylic acid (**6**)	6.30	0.10-0.50	0.25	0.016	
		0.10-0.50	0.50	0.025	
		0.10-0.50	0.75	0.033	0.045
Ethylphosphonic acid	7.97	0.025-0.10	0.50	0.014	
		0.025-0.10	0.80	0.018	0.027

[a] In water at 25 °C; ionic strength 1.0 [$(CH_3)_4NCl$]. [b] From observed pH values of buffer solutions at ionic strength 1.0 [$(CH_3)_4NCl$]. [c] Apparent rate constant in terms of total buffer concentration. [d] Approximate values (±20%) obtained using a rapid mixing syringe (see text); considerable scatter in these results was observed, presumably as a result of incomplete mixing of the carbinolamine ether with water.

amount of formation or cleavage of a particular bond. We can say that a reaction behaves *as if* there is a certain amount of charge development on a particular atom in the transition state, based on an observed Bronsted coefficient or ρ, but this measure of charge development should be used only to compare transition states with equilibria and with other transition states and not as an absolute measure of the charge on particular atoms in the transition state. Furthermore, the "effective charges" estimated in this way may not be additive, so that their sum may not be equal to the total net charge of the transition state. This is the case for the imine-forming elimination reaction described here.

The structure-reactivity comparisons for base-catalyzed elimination to form imines indicate that the reaction behaves *as if* the transition state has the distribution of "effective charges" shown in **2** (B is taken as an uncharged base in **2**). The positive charge on the catalyzing base and the negative charge on the nitrogen atom are based on previously reported Bronsted coefficients of $\beta = 0.7$ and $\beta_N = -1.0$ for substituents on the respective reacting atoms.[3,4] The data reported here establish that there is a small development of positive charge on the central carbon atom that is stabilized by electron-donating substituents on the benzene ring; the value of ρ^+, based on three points (Figure 3), is approximately −0.5. Electron-withdrawing substituents in the leaving group cause a much larger rate increase with a value of $\beta_{lg} = -1.05$ (Figure 4) that suggests a large development of negative charge on the leaving oxyanion.



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It was concluded previously that the large values of $\beta = 0.7$ and $\beta_N = -1.0$ mean that there is a large amount of proton transfer and of negative charge development on the nitrogen atom in the transition state. The imbalance between the charge development on the base and the nitrogen atom presumably reflects the localization of some positive charge on the proton in the hydrogen-bonded transition state, as in other hydrogen bonds.[21] The ionization of amines to the anion is 0.86-1.3 as sensitive to polar substituents as amine protonation,[22] the ionization constants of amides are 0.87-1.0 as sensitive to substituents as the corresponding carboxylic acids,[23] and the value of ρ for the ionization of XPhCONHPhCOOR in 20% dioxane is 1.37-1.5.[24] In spite of the fact that the large development of negative charge on nitrogen implies that there has been little electron donation from nitrogen to expel the leaving RO^- group, the very large sensitivity of the rate to electron-withdrawing substituents on the leaving group, with $\beta_{lg} = -1.05$, means that there has been a large development of negative charge on the leaving group that must reflect a con-

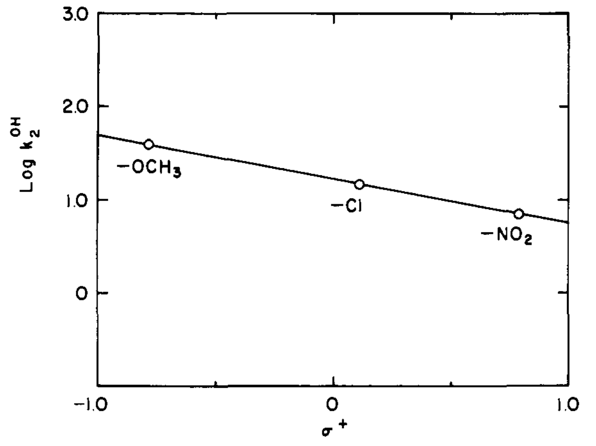
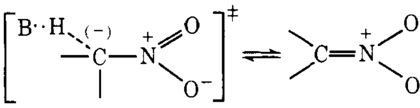


Figure 3. Dependence on σ^+ of log $k_2{}^{OH}$ for hydroxide ion catalyzed dehydration of carbinolamines derived from acethydrazide and para-substituted benzaldehydes at 25 °C, ionic strength 1.0 (KCl). The line is drawn with a slope of −0.48.

siderable amount of C–O bond cleavage in the transition state. This conclusion is confirmed by the stabilization of the transition state by electron-*donating* substituents on the benzaldehyde moiety, with $\rho^+ = -0.5$, which means that there is a net development of positive charge on the central carbon atom in the transition state. If there were no leaving of RO$^-$, the negative charge development on the adjacent nitrogen atom in the transition state would be stabilized by electron-withdrawing substituents with a ρ value of approximately +1.0, similar to the ρ value of 1.1 for the ionization of substituted 1-phenyl-2,2,2-trifluoroethanols and substituted benzylammonium ions.[25] These substituent effects establish unequivocally that the reaction does not involve rate-determining proton removal alone. The reaction is *concerted*, in the sense that both significant transfer of the proton and significant cleavage of the C–O bond have occurred in the transition state.

The surprising result is that in spite of the large negative charge on nitrogen and the development of positive charge on carbon in the transition state, there is little or no movement of electrons and negative charge on the nitrogen atom toward carbon to form the >C=N– double bond of the product imine. Evidently the reaction has proceeded to a large extent at the two ends, to transfer the proton and cleave the C–O bond, but little or not at all in the center. This implies that the carbon and nitrogen atoms maintain predominantly tetrahedral sp^3 hybridization in the transition state with little rehybridization toward the planar sp^2 structure of the imine product. It appears that the energetic advantage of maintaining significant overlap and bonding with the departing oxygen and hydrogen atoms in an sp^3-hybridized transition state is more than enough to offset the stabilization that would be achieved through the facilitation of double bond formation between carbon and nitrogen by rehybridization toward a planar sp^2 structure. This conclusion requires that in the reverse reaction, the attack of alkoxide ion on neutral >C=N–, there must be an initial rehybridization of carbon and nitrogen from sp^2 toward a pyramidal sp^3 structure accompanied by the development of a large amount of negative charge on nitrogen. Since the equilibrium constants for the overall dehydration of carbinolamine to imine show the expected stabilization of the product by electron-*donating* substituents on nitrogen ($\beta_N = 0.4$),[4] this means that starting with the imine the reaction behaves *as if* there is an increase in negative charge on nitrogen of 1.4 units by the time the transition state is reached. The situation is analogous to that in nitroalkane ionization in which there is more negative charge development on the carbon atom from which the proton is removed in the transition state than in the product and predominantly sp^3 hybridization is maintained in the transition state (eq 6); in the reverse reaction there is an



$$\left[\mathrm{B\cdot\cdot H\cdots \overset{(-)}{C}(-)(-)-\overset{+}{N}(=O)O^-}\right]^{\ddagger} \rightleftharpoons \mathrm{>C=\overset{+}{N}(O^-)_2} \tag{6}$$

initial rehybridization of carbon from sp^2 to sp^3 character accompanied by an increase in electron density in the transition state.[7] The reactions differ in that nitroalkane ionization requires the rehybridization of only a single atom.

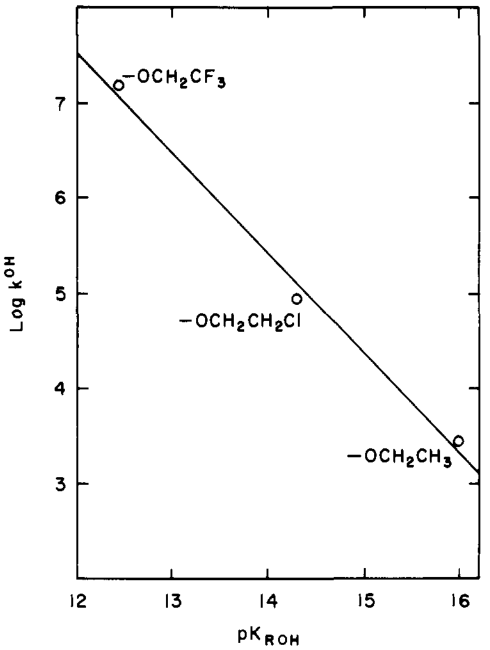


Figure 4. Dependence on the pK of the leaving alcohol[19] of log k^{OH} for hydroxide ion catalyzed alcohol elimination from α-tosylhydrazino-p-chlorobenzyl alkyl ethers at 25 °C, ionic strength 1.0 [(CH$_3$)$_4$NCl]. The line has a slope of −1.05.

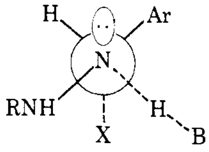
The α-secondary deuterium isotope effects, k_D/k_H, are 1.22 and 1.20 for the addition of hydroxide ion and water to protonated N-benzylidene-1,1-dimethylethylamines, respectively, and 1.20–1.31 for semicarbazone formation from benzaldehydes under conditions in which the acid-catalyzed dehydration step is rate determining. These results show that the carbon atom is close to a tetrahedral, sp^3-hybridized structure in the transition states of these reactions also.[26]

The imine-forming elimination reactions are similar to olefin-forming E2 elimination reactions of quaternary ammonium and sulfonium ions in that these carbon elimination reactions also proceed with a large amount of proton removal by the catalyzing base in the transition state, as indicated by a large ratio k_{OD^-}/k_{OH^-}, a relatively small primary deuterium isotope effect, and a large β-^{14}C isotope effect.[5,27–30] The relatively large secondary β-tritium isotope effects (k_H/k_T) in the elimination reactions of $CH_3CHTCH_2N(CH_3)_3^+$ (1.33) and p-$NO_2ArCHTCH_2N(CH_3)_3^+$ (1.20) suggest that a considerable amount of proton removal and change to sp^2 hybridization of the β-carbon atom has occurred in the transition state of these reactions.[28,29] However, the effect of polar substituents on the β-carbon atom of β-phenylethylammonium ions ($\rho = 3.7$)[30] is about half as large as for carbanion formation from substituted fluorenes ($\rho = 7.0 \pm 0.7$),[31] suggesting that there is a smaller change in "effective charge" on carbon than on the nitrogen atom of carbinolamines ($\beta_N = -1.0$). The sensitivity to substituents in the leaving group for E2 elimination of substituted tosylates ($\rho = 0.9$–1.2)[32] is also about half of that for the ionization of the related compound X-Ar-

SO_2NH_2 (ρ = 2.54),[33] which may be compared with the value of β_{lg} = −1.05 for imine-forming elimination; heavy atom isotope effects and small α-secondary deuterium isotope effects also suggest that there is relatively little bond breaking at the α-carbon atom in the transition states for E2 elimination reactions of ammonium and sulfonium salts.[5,29,30,34] E2 elimination of 1-aryl-2-phenyl-1-chloroethanes is accelerated by electron-withdrawing substituents on the α-carbon atom (ρ = 0.77),[35] in contrast to the small accelerating effect of electron-donating substituents on carbinolamine dehydration. Thus, the imine-forming elimination reactions appear to proceed with a similar amount of proton removal, less rehybridization and more buildup of negative charge on the proton-donating atom, more leaving group departure, and a greater separation of charge between the two central atoms in the transition state compared with E2 elimination reactions of carbon compounds.

Possible reasons for this difference, particularly the large development of negative charge on nitrogen, include (i) the large electronegativity of nitrogen, (ii) the poor leaving ability of hydroxide and alkoxide ions and the expectation from structure-reactivity relationships that there will be a larger charge buildup on the β carbon or nitrogen atom with poor leaving groups,[36] and (iii) the possibility that proton transfer and leaving group expulsion are orthogonal and not fully coupled.

Point iii is of particular interest, but cannot be definitively evaluated at this time because it is not known whether the proton transfer in this and related reactions takes place orthogonal to the leaving group with the driving force for the expulsion of X^- provided by the lone pair electrons of nitrogen (**3**) or anti to the leaving group as in anti E2 elimination reactions (**4**). For general acid catalysis of X^- attack on the imine in the reverse direction mechanism **4** corresponds to anti proton transfer to the position occupied by the π electrons of the double bond of the imine, whereas mechanism **3** corresponds to protonation at the site of the lone pair electrons of the nitrogen atom. It is also not known what degree of coupling or concertedness is possible if the proton transfer is orthogonal (**3**). It has usually been assumed that proton addition occurs on the lone pair electrons of nitrogen in these reactions and that coupling will be prevented by the location of the lone pair perpendicular to the plane of the entering nucleophile; in the reverse direction this mechanism makes available an unbonded lone pair of electrons on nitrogen to provide the driving force for *antiperiplanar* expulsion of the leaving group.[37] However, anti (or syn) proton transfer is also possible in imine as well as in carbon elimination reactions (**4**). If proton removal in mechanism **3** is less tightly coupled with >C=N– double bond formation than in mechanism **4**, this could help to explain the buildup of negative charge on the nitrogen atom in the transition state for carbinolamine dehydration, especially if unfavorable steric interactions between the catalyzing base and the benzene ring hinder conversion of the carbon and nitrogen atoms to planar sp^2 hybridization in mechanism **3**. A twisted transition state, analogous to that proposed for the protonation of ethylene,[38] would also avoid much of this unfavorable steric interaction.



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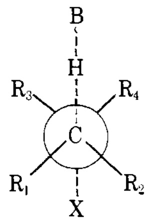

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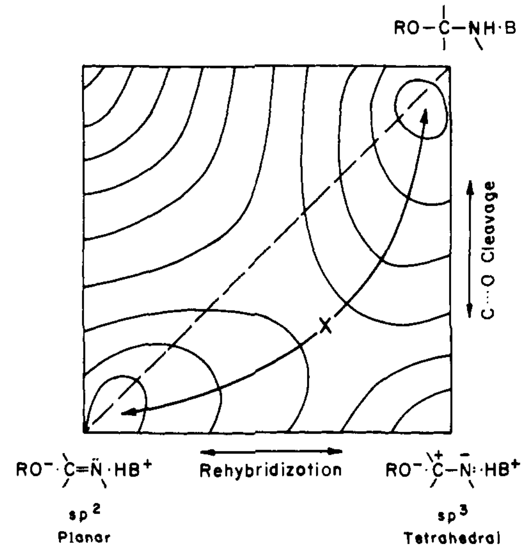


Figure 5. Reaction coordinate contour diagram to show the relationship between the amount of C–O cleavage (vertical axis) and rehybridization of the central atoms from sp^3 to sp^2 (horizontal axis) in base-catalyzed elimination reactions to form imines.

It is instructive to illustrate the interrelationships between the several processes that are occurring in reactions of this kind with reaction coordinate diagrams that have separate axes for the different processes.[36,39,40] The relationship between the proton transfer and leaving group expulsion can be shown with a contour diagram that has separate axes for each of these processes and energy in the vertical dimension, but such a diagram provides an inadequate description of carbinolamine dehydration because of the imbalance in the extent to which other processes have occurred in the transition state; a complete description would require a separate dimension for each process. Following Critchlow's suggestion for nitroalkane ionization[40] the relationship between leaving group expulsion and rehybridization in carbinolamine dehydration is illustrated by the diagram of Figure 5; other processes are taken as being in their lowest energy state along the reaction coordinate. The horizontal axis describes the change of the carbon and nitrogen atoms from tetrahedral sp^3 hybridization on the right to a planar geometry and sp^2 hybridization on the left (assuming that these changes are synchronous), and the vertical axis describes the amount of O–C bond cleavage. The structure in the upper left corner is energetically inaccessible, because it requires tetravalent or pentavalent carbon with planar sp^2 hybridization. A diagonal reaction coordinate, shown by the dashed line, describes a balanced reaction in which rehybridization is closely coupled to alkoxide expulsion. The data suggest that the reaction follows a path (curved line) in which rehybridization lags behind alkoxide expulsion in one direction and is ahead of carbon–oxygen bond formation in the reverse direction. Such a reaction coordinate is reasonable because it avoids the high-energy region in the upper left corner and allows stabilization of the transition state by partial formation of the C–O and N–H bonds. The sp^3-hybridized pyramidal structure in the lower right corner is shown as an energy maximum rather than as a metastable intermediate, based on the assumption that there is no activation barrier for rehybridization to the planar, sp^2 structure.

INDO calculations for the gas-phase addition of ammonia to formaldehyde suggest that there are differences in the extent to which the various geometric and electronic components change during the course of the reaction,[41] but the differences are smaller than the degree of imbalance indicated by the substituent effects reported here.

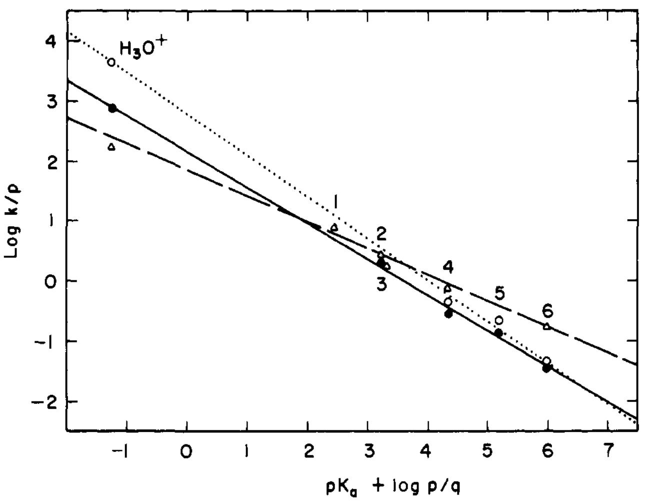
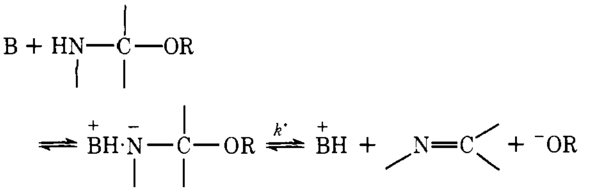


Figure 6. Bronsted plots for general acid catalysis of the elimination of alcohols, ROH, from α-tosylhydrazino-*p*-chlorobenzyl alkyl ethers by hydronium ion and carboxylic and cacodylic acids. Statistical corrections have been made according to the method of R. P. Bell and P. G. Evans (*Proc. R. Soc., Ser. A*, **291**, 297 (1966)). Acid catalysts are identified in Table V. Least-squares slopes of the lines are −0.69 for the ethyl ether (○, dotted line), −0.60 for the 2-chloroethyl ether (●, solid line), and −0.44 for the 2,2,2-trifluoroethyl ether (△, dashed line).

Finally, we consider the status of the leaving RO^- group in the transition state. If the alkoxide group had left completely to form a carbonium ion, the transition state would be stabilized by electron-donating substituents with a value of ρ^+ near −4.6 to −5.6, the values for the solvolysis of substituted benzyldimethylchlorides and for the equilibrium formation of monosubstituted diphenylmethane carbonium ions, respectively.[42] A correction of +1 unit for a full negative charge on the adjacent nitrogen atom, based on $\rho = 1.1$ for the dissociation of substituted benzylammonium ions and 1-phenyl-2,2,2-trifluoroethanols,[25] would not bring these values close to the observed value of $\rho = -0.5$. This suggests that the alkoxide ion has *not* left completely and that in spite of the value of $\beta_{lg} = -1.05$ there must still be significant bonding between the leaving alkoxide ion and the central carbon atom in the transition state. The value of β_{nuc} for the attack of alkoxide ions in the reverse direction is ~0, similar to the small values of $\beta_{nuc} \sim 0.2$ for the attack of alkoxide ions on phenyl esters and thiol esters.[43] However, the much larger value of $\beta_{nuc} = 0.7$ for rate-determining attack of phenoxide ions on esters and thiol esters indicates that there is a large amount of C–O bond formation in the transition state for the attack of these oxyanions, and it has been suggested that the smaller value of β_{nuc} for alkoxide ions may be a consequence of the stronger solvation of the more localized negative charge of alkoxides.[43] The observed value of β_{nuc} represents a balance between desolvation of the nucleophile, which is aided by electron withdrawal, and nucleophilic attack, which is aided by electron donation; in the reverse reaction, solvation of the developing alkoxide anion lags behind C–O bond cleavage and accounts for the large value of $\beta_{lg} \cong -1.5$ in acyl group reactions. The same hypothesis makes it possible to reconcile the values of $\beta_{lg} = -1.05$ and $\beta_{nuc} \sim 0$ in the imine reaction with the ρ^+ value of −0.5 that suggests the existence of significant C···O bonding in the transition state. Thus, alkoxide expulsion and attack represents another example of imbalance between the extent to which different processes have taken place in the transition state, and the available data are consistent with the hypothesis that this imbalance is between the development of solvation and the amount of C–O bond cleavage during alkoxide expulsion.

Mechanism. The results described so far establish that there has been a large amount of proton transfer and RO^- expulsion in the transition state but do not distinguish between a fully concerted mechanism and a stepwise mechanism in which proton transfer occurs first to form a hydrogen-bonded intermediate with the proton in a potential well, followed by expulsion of RO^- with little or no motion of the proton along the reaction coordinate in the transition state (eq 7). Although the formation of a free amine anion as an intermediate can be excluded,[4] an anion that is hydrogen bonded to BH^+ would be more stable and must be considered as a possible intermediate in a stepwise, "preassociation" mechanism (eq 7). A crude estimate of the expected behavior of such a mechanism gives results that are not inconsistent with the experimental results. Hine has proposed eq 8 to provide an estimate of the association constant K_{AB} for the formation of a hydrogen bonded complex between AH and B in water.[44] If the transition state for the attack of hydroxide ion on *p*-chlorobenzaldehyde acethydrazone has a pK of 14, eq 8 predicts a Bronsted α value of 0.38 for transition state stabilization by hydrogen bonding to general acids, which may be compared with the observed value of $\alpha = (1 - \beta) = 0.28$ for this reaction.[4] The calculated ratio of the catalytic constants for protonated quinuclidinol, k_Q, and water, k_{HOH}, is then $K_{AB} = k_Q/k_{HOH} = 2.4\ M^{-1}$, compared with the observed ratio of 4.7 M^{-1}. In view of the approximate nature of eq 8, these values suggest that a hydrogen bonding mechanism could account for the observed catalysis.


(7)

$$B + HN{-}C{-}OR \rightleftharpoons \overset{+}{B}H\cdot\overset{-}{N}{-}C{-}OR \overset{k'}{\rightleftharpoons} \overset{+}{B}H + {>}N{=}C{<} + {}^{-}OR \quad (7)$$

$$\log K_{AB} = 0.024(pK_{HA} - pK_{H_2O}) \times (pK_{H_3O^+} - pK_{BH^+}) - \log 55 \quad (8)$$

However, other considerations suggest that although hydrogen bonding certainly provides stabilization for the transition state, the reaction mechanism is concerted rather than stepwise. Based on an estimated pK_a of 27 ± 2 for the carbinolamine nitrogen atom[4] the rate constant $k' = k_2^{OH}K_w/K_a$ for breakdown of the intermediate anion hydrogen bonded to water must be $10^{14\pm2}\ s^{-1}$ and the corresponding value for the *p*-methoxybenzaldehyde compound must be $10^{15\pm2}\ s^{-1}$ in order to account for the observed values of k_2^{OH} in Table III. A similar calculation[45] for the trifluoroethyl ether of the *p*-chlorobenzaldehyde-*p*-toluenesulfonylhydrazide adduct gives a value of $k' = 10^{16\pm2}\ s^{-1}$. Thus, the lifetime of the "intermediate" is less than that of a bond vibration, so that the "intermediate" cannot exist, and the reaction *must* proceed through a concerted mechanism. The large difference of 18 units between the pK_a of 27 for the NH of the acethydra-

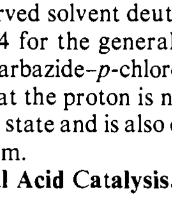
Table VI. Variation in Bronsted α Values for General Acid Catalysis of Alcohol Elimination from Carbinolamine Ethers and Phthalimidium Adducts (**5**)

		Bronsted α	
ROH	pK_a[a]	Carbinolamine ether	Phthalimidium adduct[b]
CF_3CH_2OH	12.37	0.44	0.49
$ClCH_2CH_2OH$	14.31	0.60	0.64
CH_3CH_2OH	16.0	0.69	0.74

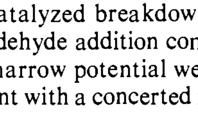
[a] Reference 19. [b] Reference 15b.

zide-*p*-chlorobenzaldehyde addition compound[4] and the pK of 9 for triethylenediamine monocation is also difficult to reconcile with a stepwise hydrogen-bonding mechanism in which the proton is in a stable potential well. With a favorable ΔpK of 18 units it is unlikely that there is a significant barrier for proton transfer from triethylenediamine cation to the nitrogen anion of the carbinolamine in a hydrogen-bonded ion pair "intermediate" of the triethylenediamine-catalyzed reaction (eq 7). If there is no such barrier the reaction cannot proceed through a stepwise mechanism and must be concerted. The observed solvent deuterium isotope effect of $k_{H_2O}/k_{D_2O} = 3 \pm 0.4$ for the general base catalyzed breakdown of the thiosemicarbazide-*p*-chlorobenzaldehyde addition compound[3] means that the proton is not in a narrow potential well in the transition state and is also consistent with a concerted reaction mechanism.

General Acid Catalysis. In contrast to the base-catalyzed reaction, the general acid catalyzed expulsion of alcohols from α-tosylhydrazino-*p*-chlorobenzyl alkyl ethers shows only a small or no increase in rate with electron-withdrawing substituents on the leaving alcohol (Figure 6). As the strength of the catalyzing acid is decreased there is a decrease in the sensitivity of the rate to substituents in the leaving group, and the rate of the proton-catalyzed reaction is *decreased* by electron-withdrawing substituents. There is a corresponding decrease in the Bronsted slope α with electron-withdrawing substituents on the leaving group, from 0.69 for the ethyl ether to 0.44 for the 2,2,2-trifluoroethyl ether (Table VI). The rate constant for catalysis by the proton appears to fit on the same Bronsted line that correlates the rate constants for weaker acids; the same result was found for the analogous reaction of **5** but the proton exhibits a significant negative deviation for the acid-catalyzed expulsion of substituted phenols from **6**.[15b,46] The change in α with changing pK of the leaving group and the change in β_{lg} with changing acid strength are described by eq 9 with a Cordes coefficient[36,47] of $1/c_5 = 0.05$. This value is similar to the value of $1/c_5 = 0.07$ for the hydrolysis of **5** and is smaller than the value of approximately 0.2 for the hydrolysis of **6**.



5



$C_6H_5-\overset{H}{\underset{OC_6H_4X}{C}}-OCH_3$

6

$$\Delta\alpha/\Delta pK_{lg} = 1/c_5 = -\Delta\beta_{lg}/\Delta pK_{HA} \qquad (9)$$

The decreased sensitivity to the pK of the leaving group with stronger acid catalysts and, in particular, the change to an inhibition of the proton-catalyzed reaction by electron-withdrawing substituents means that proton transfer to the leaving alcohol must play a significant role in the reaction. The gradual change in α and the change in both magnitude and direction of the substituent effect in the leaving group are inconsistent with a stepwise reaction mechanism and provide evidence in support of a concerted mechanism in which both proton transfer and carbon-oxygen bond breaking play a significant role in the transition state, as has been discussed previously for the reactions of **5** and **6**.[15b,46]

In this type of reaction the transition state adjusts to "take advantage" of a substituent on the central atom so that, for example, an electron-donating substituent on the leaving alcohol leads to a change in transition state structure such that there is more proton transfer to the oxygen atom and an increase in α. Similarly, a stronger acid leads to a change in the balance between C-O bond breaking and proton transfer to the leaving alcohol such that there is more positive charge on the oxygen atom and an increased (more positive) β_{lg}. These interrelationships can be conveniently illustrated with three-dimensional reaction-coordinate diagrams that have separate axes for proton transfer and C-O cleavage.[36,39,40] The earlier finding that α for acid-catalyzed carbinolamine dehydration increases with electron-withdrawing substituents on the nitrogen atom (the value of the Cordes coefficient $1/c_2$ is 0.02)[4] requires that there be a diagonal component to the motion along the reaction coordinate in the transition state. All of the available data are consistent with a direction of the reaction coordinate that is intermediate between diagonal and vertical, with significant motion along both axes in the transition state. The absence of a regular decrease in β_{lg} with electron-withdrawing substituents on the leaving group in this class of reactions[15b,46] suggests that the reaction coordinate motion is not strictly diagonal.

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Equilibria and Kinetics of Disproportionation of Barium Salts of Radical Anions of Tetraphenylethylene and Tetracene

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Abstract: Disproportionation of barium salts of radical anions of tetraphenylethylene, TPE, and tetracene, T, was investigated in THF and DME. The disproportionation constant for the reaction $Ba^{2+},TPE^{\cdot -} + TPE^{\cdot -} \rightleftarrows Ba^{2+}, TPE^{2-} + TPE$ is very high in both solvents, apparently greater than 10^6. The bimolecular rate constant of that reaction taking place in DME was found to be $\sim 10^7\ M^{-1}\ s^{-1}$, the kinetics was studied by flash photolysis technique. The disproportionation constant of $Ba^{2+},T^{\cdot -} + T^{\cdot -} \rightleftarrows Ba^{2+},T^{2-} + T$ in THF was found to be ~520, a lower value of ~20 being found in DME. Since the dissociation constant of $Ba^{2+}(T^{\cdot -})_2$ in THF was determined at 6×10^{-6} M, the disproportionation constant of the reaction $T^{\cdot -}, Ba^{2+},T^{\cdot -} \rightleftarrows T + Ba^{2+},T^{2-}$ is 3×10^{-3} M. Kinetics of the disproportionation of $Ba^{2+},T^{\cdot -} + T^{\cdot -}$ was investigated in THF, again by flash-photolytic technique. The results indicate that this reaction proceeds through two routes: (a) (k_a) $Ba^{2+},T^{\cdot -} + T^{\cdot -} \rightleftarrows Ba^{2+},T^{2-} + T$ with $k_a = 6 \times 10^8\ M^{-1}\ s^{-1}$, and (b) $T^{\cdot -} + Ba^{2+},T^{\cdot -} \rightleftarrows T^{\cdot -},Ba^{2+},T^{\cdot -}$, followed by $T^{\cdot -},Ba^{2+},T^{\cdot -} \rightleftarrows T + Ba^{2+}, T^{2-}$. The merits of this mechanism were discussed. Finally, some striking features of the optical spectrum of Ba^{2+},TPE^{2-} were reported. Their interpretation led us to postulate an unsymmetric structure of the barium salt, namely, $Ba^{2+},Ph_2\overline{C}-\overline{C}Ph_2$, with the cation strongly associated with one but not with the other $-\overline{C}(Ph)_2$ chromophore.

Following our studies of the effect of alkali counterion and of solvent on the equilibrium and rates of disproportionation of radical anions,[1-4] we investigated now the disproportionation of the barium salts of radical anions derived from tetraphenylethylene, TPE, and tetracene, T. The salts of the respective dianions were prepared in THF or DME by reacting solution of the appropriate hydrocarbon with a barium mirror, the latter being formed by the procedure described by Sigwalt et al.[5] All the operations and the subsequent handling of the solutions were performed in high vacuum.

Barium Salts of Radical Anions and Dianions of Tetraphenylethylene. THF or DME solutions of tetraphenylethylene, TPE, contacted with a barium mirror yield the salt of the dianion, Ba^{2+},TPE^{2-}. The disproportionation of the pertinent radical anions is high and only a weak ESR signal could be detected from DME solutions of $\sim 2 \times 10^{-4}$ M Ba^{2+},TPE^{2-} in the presence of $\sim 5 \times 10^{-3}$ M of the unreduced TPE. On this basis the disproportionation constant in DME is estimated to be $\sim 10^6$. The optical spectrum of Ba^{2+},TPE^{2-}, shown in Figure 1, is unaffected by dilution from $\sim 10^{-4}$ to 10^{-6} M. The λ_{max} of the absorption band peaking at 485 nm is unaffected by the solvent. This band appears in the spectra of the sodium salt, $TPE^{2-},2Na^+$ (λ_{max} 485 nm) and the free TPE^{2-} ion formed when the sodium salt is dissolved in hexamethylphosphorictriamide (HMPA). The strong band appearing at shorter wavelength (λ_{max} 345 nm in THF and 350 nm in DME) is absent in the other two spectra, but a similar band (λ_{max} 385 nm) is pronounced in the spectrum of the lithium salt, $TPE^{2-},2Li^+$. Its appearance in the spectrum of the lithium salt, in addition to the "conventional" band (λ_{max} 495 nm), was discussed elsewhere.[6] These two bands do not originate from the chromophore's splitting[7] because the lithium or sodium salts of 1,1,4,4-tetraphenylbutane dianions,

$$Cat^+, \overline{C}(Ph)_2CH_2CH_2\overline{C}(Ph)_2,Cat^+$$

with chromophores identical with those of TPE^{2-}, but placed further apart, again absorb only at ~480 nm and not at ½(385 + 495) = 440 nm. Moreover, the 385-nm band disappears on addition of tetraglyme to the THF solution of $TPE^{2-},2Li^+$ (see ref 6).

The appearance of the new band (385 nm) in the spectrum of $TPE^{2-},2Li^+$ was rationalized[6] by postulating that one of the $-\overline{C}Ph_2$ groups of this skewed-shape salt is tightly associated with Li^+, while the other Li^+ cation is fully solvated and forms a loose ion pair with the second chromophore. The latter pair absorbs like the free $-\overline{C}Ph_2$ anion or the loose sodium salt, i.e., at ~495 nm, whereas the absorbance of the very tight pair is substantially shifted to the shorter wavelength, giving rise to the 385-nm band. Indeed, the integrated extinction coefficient of the 485-nm band of the free TPE^{2-} anion or its loose sodium aggregate is twice as high as that of the 495-nm absorption band of the lithium salt. Other evidence reported in ref 6 corroborates this explanation.

A somewhat similar explanation may account for the