J. Phys. Chem. A **2007,** *111,* 12871−12877

ARTICLES

Equilibrium Constants in Reactions of 2-Aminoethanol and Ammonia with Isophthalaldehyde and Terephthalaldehyde

E. Kulla and P. Zuman*

Department of Chemistry, Clarkson University, Potsdam, New York 13699-5810

Received: July 16, 2007; In Final Form: September 17, 2007

Equilibria established in reactions between isophthalaldehyde (IPA) and terephthalaldehyde (TPA) on one side and 2-aminoethanol and NH_3 on the other side were followed in solutions, where these amines acted both as reagents and as buffers. The equilibrium between TPA and 2-aminoethanol was followed spectrophotometrically; all others, of reactions of TPA with NH_3 and of IPA with both NH_3 and $H_2N-CH_2-CH_2-OH$, were followed by using polarography. Separate limiting reduction currents of the dialdehyde and its imine enable simultaneous determination of the starting material and the product. The equilibria are shifted more in favor of the imine in reactions of TPA than those of IPA. Equilibrium constants for reactions of both TPA and IPA with 2-aminoethanol are 3 orders of magnitude higher than those observed for the reactions of dialdehydes with NH_3, even when the pK_a values of these two reagents differ only slightly.

Introduction

To contribute to the elucidation of processes involved in the reaction of orthophthalaldehyde with amino acids that found an extensive analytical application,[1] the reactions of the three isomeric phthalaldehydes with primary amines are investigated. Such reactions with the 1,2 isomer are complicated by the possibility of formation of an annelled five-membered ring and will be dealt with separately. In this contribution, the reactions of the 1,3-benzenedicarboxaldehyde (isophthalaldehyde, IPA) and the 1,4-benzenedicarboxaldehyde (terephthalaldehyde, TPA) are discussed. As reacting nucleophiles, ammonia as the structurally simplest representative and 2-aminoethanol were chosen. The latter compound was selected in view of its limited volatility, high solubility in aqueous solutions, and high reactivity as a nucleophile. Moreover, the absence of the carboxylate grouping, encountered in amino acids, eliminates the role of Coulombic interactions.

All discussed reactions have been followed in solutions containing an excess of the amine, compared with the concentration of the dicarboxaldehyde. In most instances, the mixture of the amine and its protonated form served at the same time as a reagent, as a buffer, and as a supporting electrolyte in electroanalytical investigations. Only at the lowest concentrations of the mixture of the amine and its salt, a solution of a buffer was added to control the pH. As borate buffers were found to react with components of the reaction mixture, particularly with carbinolamine intermediates, buffers prepared from 4-hydroxybenzenesulfonic acid[2] were used. These buffers enabled a constant pH within p$K_a \pm 1.0$ of the amine used. To follow equilibria in reaction mixtures containing the carbonyl compounds and amines, measurements of polarographic limiting currents were used in most instances. Such application was made possible in most cases by the presence of well-formed separate waves of reductions of carbonyl and azomethine groups. As has been reported earlier,[3] the reduction of the azomethine bond usually takes place at potentials more positive than that of the carbonyl group in the corresponding aldehyde or ketone. When this condition is fulfilled, a simultaneous determination of the carbonyl group in a substituted benzalaldehyde and of the product of its reaction with the amine is possible. This condition was fulfilled in this study with a single exception:

For reactions of both dicarboxaldehydes with ammonia, similarly as for additions of 2-aminoethanol to IPA, 4-chlorobenzaldehyde, and benzaldehyde, the reduction of the imine occurs at more positive potentials than that of the parent aldehyde. Similarly, two separated waves were observed in the presence of amines in the reactions of aromatic aldehydes, resulting in two two-electron reductions in solutions of both IPA and TPA. Such behavior enabled the use of polarography for following these reactions by measuring the limiting currents of the resulting imines and of the parent aldehydes.

Such separation of waves of the reductions of the aldehyde and of the imine was not observed for the reaction of TPA with 2-aminoethanol. This was attributed to a compensation of two opposing structural effects. In this reaction, nevertheless, the application of spectrophotometry was successful, even when its use in investigation of the other reactions was limited.

Addition of amines to carbonyl compounds involves formation of a carbinolamine intermediate. The use of polarography has recently been proven useful for the experimental evidence of this intermediate in reaction of benzaldehyde[4] and terephthalaldehyde[5] with hydrazine.

Experimental Section

Instrumentation. A Sargent-Welch Model 4001 polarograph was used for recording direct current (DC) current−voltage

---

* To whom correspondence should be addressed. E-mail: zumanp@clarkson.edu. Phone: (315) 268-2340. Fax: (315) 268-6610.

10.1021/jp0755692 CCC: $37.00

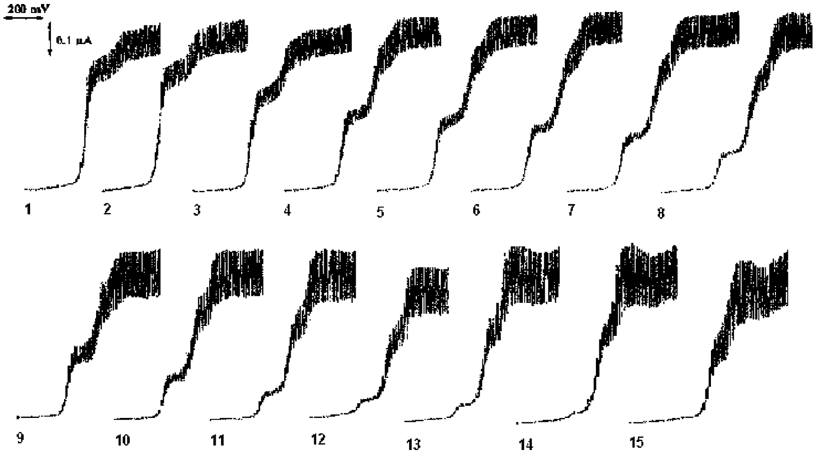


Figure 1. Polarographic current−voltage curves in solution containing 0.1 mM isopthalaldehyde and concentration of 2-aminoethanol varying from 30 to 0.05 mM at pH 9.5 dilluted with borate buffer pH 9.5: (1) 30, (2) 20, (3) 10, (4) 5, (5) 4, (6) 2.5, (7) 2, (8) 1.5, (9) 2.5, (10) 1.5, (11) 1, (12) 0.5, (13) 0.4, (14) 0.2, and (15) 0.05 mM 2-aminoethanol. Curves recorded from −0.6 V.

curves. The electrolysis was carried out in a Kalousek cell,[6] in which the analyzed solution, containing the dropping mercury electrode (DME), was separated by a liquid junction from the reference cell compartment containing a saturated calomel electrode (SCE). The DME, which was placed in the analyzed solution, had a droptime $t_1 = 4$ s and $m = 2.2$ mg·s^{-1} at $h = 49$ cm.

UV−vis absorption spectra were recorded using a Hewlett-Packard Agilent 8453 UV−vis spectrophotometer with a fused quartz cell with 10 mm path length. For the pH measurements, a Denver Instruments, model UB-10, pH meter equipped with a glass electrode was used.

Materials. Isophthalaldehyde (IPA), terephthalaldehyde (TPA), and 4-chlorobenzaldehyde were purchased from Aldrich and benzaldehyde was obtained from J. T. Baker. Acetonitrile, supplied by J. T. Baker, was used to prepare 0.01 M stock solutions of the above listed compounds.

Boric acid, sodium and ammonium chloride, ammonia, and sodium hydroxide for the preparation of buffers were reagent-grade chemicals obtained from J. T. Baker; 2-aminoethanol, 2-aminoethanol hydrochloride, and the sodium salt of 4-hydroxybenzenesulfonic acid were purchased from Aldrich.

Solutions of buffers containing 2-aminoethanol were preferably prepared from the hydrochloride salt, as the 99% ethanolamine Reagent Plus from Aldrich contained zinc ions and another reducible impurity, manifested by reduction waves on polarographic *i*−*E* curves.

Solutions. 0.01 M stock solutions of TPA, IPA, 4-chlorobenzaldehyde, and benzaldehyde were prepared in acetonitrile. All stock solutions were stored in a refrigerator in the dark for up to two weeks.

To follow the role of the concentration of the basic form of the amine at constant pH, buffers based on ammonia or 2-aminoethanol were prepared by using the same ratios of the amine and the ammonium form and varying concentration of the amine, mostly at pH 9.3 for ammonia and pH 9.5 for 2-aminoethanol. At low concentrations of the ammonium form, the pH was kept constant by addition of a borate or 4-hydroxybenzenesulfonate buffer of the same pH.

For investigation of the role of pH, the concentration of the amine was kept constant, and the concentration of the protonated form of the amine was varied.

Procedures. To record polarographic *i*−*E* curves, 0.1 mL of a 0.01 M stock solution of the dicarboxyaldehyde or benzaldehyde was added to 9.90 mL of the buffer solution, the pH of which was measured to be within ±0.05 pH unit of the chosen value. The glass electrode used was calibrated using standard buffers containing 1% acetonitrile similar to the studied solutions.

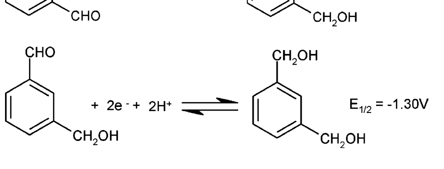
For experiments where the buffer concentration was varied, a solution of potassium chloride was added to keep the ionic strength constant. Polarographic current−voltage curves were recorded after purging with N_2 for removal of oxygen for about 3 min.

For the recording of absorption spectra in the UV region, 0.1 mL of a 0.01 M stock solution was added to 9.90 mL of a buffer solution.

In all initial experiments, the dependence of the limiting current or absorbance was measured as a function of time, and establishment of equilibria was verified.

Results and Discussion

Reactions of Isophthalaldehyde (IPA). In sulfonate and borate buffers between pH 8.3 and 10.5, IPA is reduced[7] in two two-electron waves denoted i_1 and i_2 at −1.16 V (1) and −1.30 V (2). In this pH range, the half-wave potentials of both waves are practically pH independent, as the reduction involves unprotonated species.

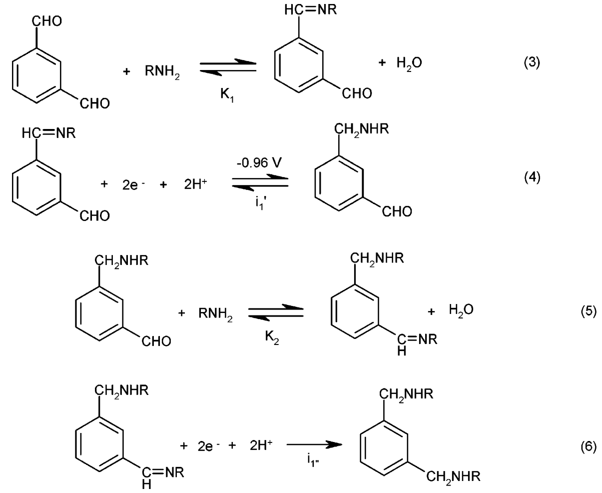


(1)

(2)

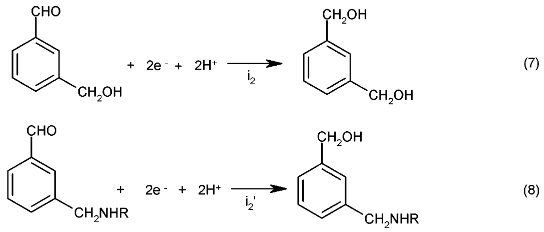
In the presence of 2-aminoethanol (RNH_2) an additional wave i_1' at −0.96 V increased with increasing concentration of the amine (Figure 1). This wave (i_1') reached a limiting value, corresponding to a two-electron reduction of an imine (4), formed in the reaction of IPA with one mole of RNH_2 (3).

With a further increase in the amine concentration, wave i_1' was overlapped by wave i_1'' with a half-wave potential of −1.03 V. This wave is attributed to the reduction of an imine (6) that is formed in the reaction of the amine (5) with the reduction product resulting in reaction 4. Hence, processes occurring in wave i_1'' are described by eqs 5 and 6:

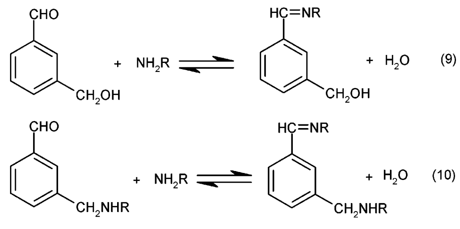


The presence of two consecutive reactions of a carbonyl group with an amine 3 and 5 is supported by the shape of the plot of (i_1[+ i_1'') as a function of log [RNH_2] (Figure 2). This shape clearly indicates the presence of two equilibria, one with an equilibrium constant K_1 = [monoimine]/[dialdehyde] [RNH_2] = 4.2×10^2 L mol^{-1}, the other with K_2 = [substituted imine]/[substituted benzaldehyde] [RNH_2] = 1.1×10^2 L mol $^{-1}$. Larger value of K_1 reflects the larger substituent effect of 3-CHO ($\sigma_{3-CHO} = 0.36$) than that of 3-CH_2NHR ($\sigma_{3-CH_2NH_2} = 0.03$, $\sigma_{3-CH_2NH_3^+} = 0.32$), as at pH 9.5 the amine is present half in the protonated form, so $\sigma_{average} \approx 0.15$.

The increases in waves i_1' and i_1'' are accompanied by a decrease in the most negative wave i_2 at −1.30 V. In this wave, the aldehydic groups in 3-formylbenzyl alcohol (7) and 3-formylbenzylamine derivative (8) are reduced in a two-electron step.



Evidently, the substituent effects of 3-CH_2OH and 3-$CH_2NHCH_2CH_2OH$ are too similar to show a significantly different effect on the potential of the formyl group. The shape of the plot of i_2 on pH is similar to that of the dependence of i_1 = f (pH; Figure 3). But the difference between the two plots supports the interpretation that in wave i_2 also the reduction of the 3-formylbenzylamine derivative (8) i_2' contributes to the measured limiting current. A discussion continues for the reduction path of imines formed by reaction of the amine with aldol (9) and with the 3-formylbenzalamine derivative (10):



Both these imines are reduced in a single two-electron step i_2' (11, 12):

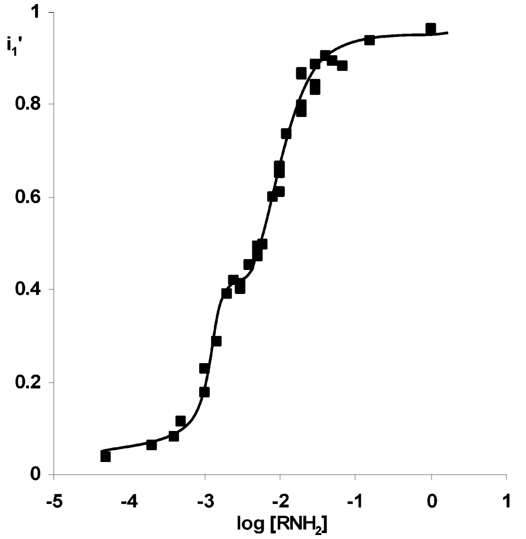


Figure 2. Dependence of the wave (i_1' μA) of the reduction of the 0.1 mM solution of monoimine of isophthalaldehyde on logarithm of concentration of 2-amimoethanol (RNH_2, ■).

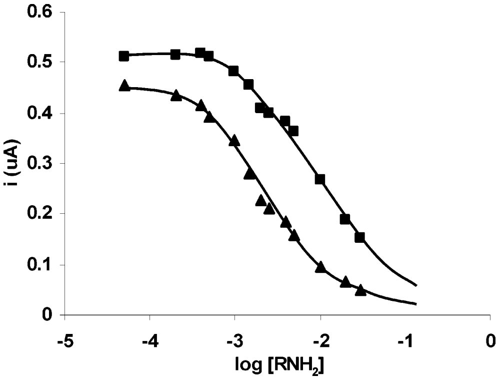
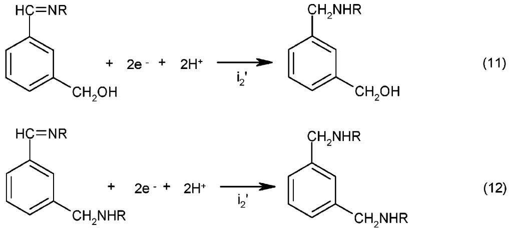


Figure 3. Dependence of the decrease of the first reduction wave i_1(▲) in solution of 0.1 mM isophthalaldehyde and of wave i_2 (■), corresponding to the reduction of the second wave of isophthalaldehyde and the reduction of the 3-amino-methylbenzaldehyde, resulting from the reduction of the monoimine of the isophthalaldehyde on logarithm of concentration of 2-aminoethanol.



As in reactions 7 and 8, the difference in potentials of processes 11 and 12 are too small to result in a separation of the two waves. Moreover, the potential of the resulting wave i_2' at about −1.2 V is too close to the potential of wave i_1 at −1.16 V, and thus wave i_2' overlaps wave i_1. This is a result of two different structural effects: In the addition 3, the reaction of the first formyl group is facilitated by the presence of a 3-CHO group as a substituent. In reactions 11 and 12, the effect of substituents 3-CH_2OH and 3-$CH_2NHCH_2CH_2OH$ are too small, but the replacement of the reduced group CH═O in eq 3 by the reduced group CH═NR in eqs 11 and 12 results in a shift of these reductions to more positive potentials. As a result of these different factors, there is an overlap of waves i_1 and i_2'. As a result, the sum of currents ($i_1 + i_1' + i_1'' + i_2 + i_2'$) remains constant.

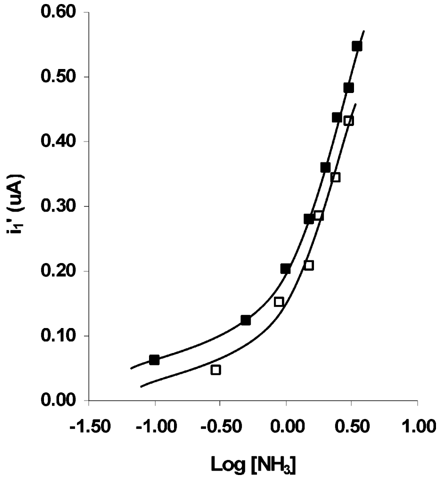
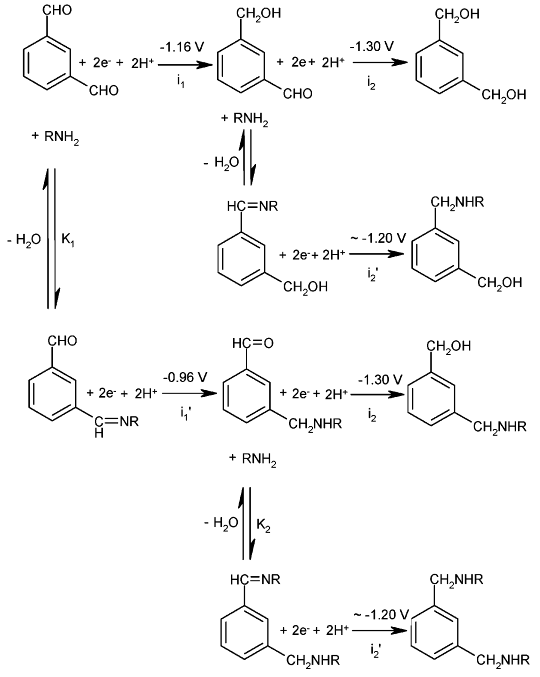


Figure 4. Dependence of the limiting current i_1', corresponding to a reduction of the monoimine in 0.1 M solution of isophthalaldehyde on logarithm of concentration of ammonia−ammonium chloride buffer pH 9.3. ■ Ionic strength kept constant by addition of potassium chloride; □ ionic strength varied with concentration of the buffer.

SCHEME 1



The reduction of imines formed in the presence of IPA in reactions 9 and 10 is supported by comparison with the behavior of the imines of other benzaldehydes. Such imines were generated in reactions of benzaldehyde and 4-chlorobenzaldehyde with 2-aminoethanol. Both of their half-wave potentials were in the same potential range as those of wave i_2', but the dependence of their current i_1' on log [RNH_2] was close to that of wave i_2' of OPA.

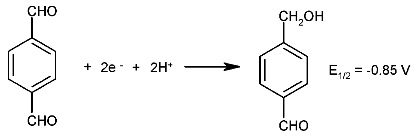
When the pH was changed in the reaction mixture by varying the ratio [RNH_2]/[RNH_3^+], but keeping the [RNH_2] constant, the ratio of $i_1'/(i_1' + i_1 + i_2)$ did not change. Hence, the value of the equilibrium constant K_1 was confirmed to be pH independent.

The overall scheme of reactions of IPA in the presence of 2-aminoethanol and accompanying reactions is given in Scheme 1.

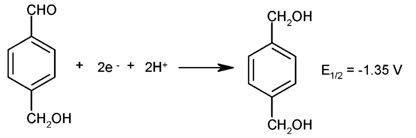
As the ammonia (NH_3) is a much weaker nucleophile than $H_2NCH_3CH_2OH$, the reaction of IPA with ammonia had to be studied at much higher concentration of ammonia than was possible in solutions containing 2-aminoethanol. As the concentration of ammonium chloride was limited by its solubility, it was not possible to achieve a practically complete conversion into imine, as was possible with 2-aminoethanol. Thus, instead of a graphical method, a numerical one with a more restricted number of useful experimental data (Figure 4) had to be used for calculation of the equilibrium constant.

In a solution containing 1.0−3.0 M NH_3 and an identical concentration of ammonium chloride, an increase in wave i_1' was observed at −0.88 V, more positive than the wave of unreacted IPA at −1.11 V (Supporting Information 1). Using the expression $K = i_d/(i_d - i_1')\,[NH_3]$, an average equilibrium constant $K = 0.7 \pm 0.1$ was found. These experiments were carried out both in solutions where the ionic strength was varied by variation of [NH_4^+] from 1.0 to 3.5 and in those where the ionic strength was kept constant at 3.5 by addition of potassium chloride, but the difference was not marked (Figure 4), as can be expected for a reaction between two uncharged species.

Reactions of Terephthalaldehyde (TPA). In the investigated pH range, in a 4-hydroxybenzenesulfonate buffer, terephthalaldehyde (TPA) is reduced[8] in two steps, i_1 and i_2. In the first step, i_1, one of the two aldehydic groups in TPA is reduced at −0.85 V in reaction 13 that involves an overall transfer of two electrons. In the second wave, i_2, the remaining formyl group undergoes reduction at −1.35 V (14).

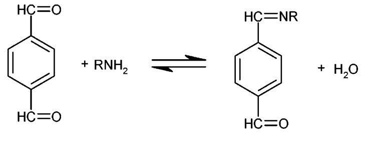


(13)

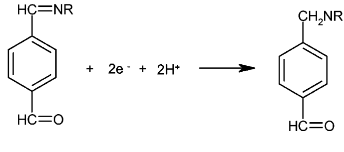


(14)

The limiting currents of the first two-electron step, which actually takes place in two ill-separated one-electron waves, as well as the half-wave potentials, remain practically unaffected in the presence of 2-aminoethanol (Supporting Information 2). As both spectrophotometry (see below) and the behavior of the second two-electron step proved formation of an imine, it follows that in the wave i_1 both the first formyl group of TPA is reduced (13) and the reduction of the imine (16) formed in reaction 15 takes place.



(15)



(16)

This behavior is in contrast to that observed for reactions of other substituted benzaldehydes with ammonia, alkylamines, 2-aminoethanol, or glycine.[3] The imines formed in these reactions, which are reduced in protonated form, undergo reductions at more positive potentials than the parent carbonyl compounds. The transfer of electrons to a $C{=}NH^+$ group requires thus lower energy than the transfer to the $C{=}O$ groups.

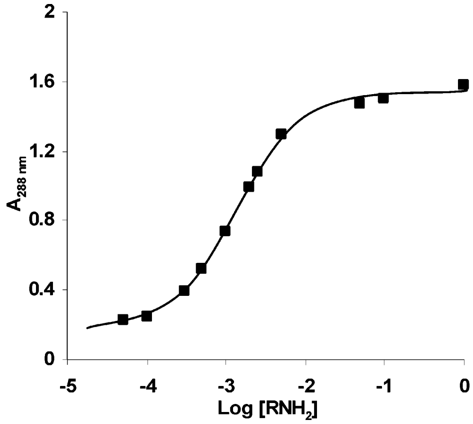


Figure 5. Dependence of absorbance at 288 nm in solution of 0.1 mM terephthalaldehyde on logarithm of concentration of 2-aminoethanol, used also as a buffer at pH 9.5 (■).

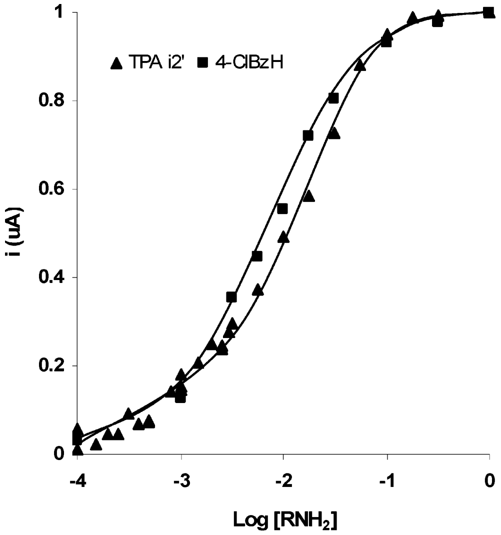


Figure 6. Comparison of dependence of wave i_2' (▲) in solution of 0.1 mM terephthalaldehyde, which corresponds to reduction of 4-CH_2-OH and 4-CH_2NH_2 substituted benzaldehydes, formed by reduction of the dialdehyde and its monoimine on logarithm of concentration of 2-aminoethanol (RNH_2) with wave i_1' of the imine formed in solution of 0.1 mM 4-chlorobenzaldehyde (■).

In this aspect, the reaction of 2-aminoethanol with IPA (discussed above) follows the general pattern and differs from the reaction with TPA.

The absence of separation of waves of the imine and the carbonyl group in the reaction of TPA is attributed to a compensation of two opposing effects: Whereas the replacement of C=O by $C{=}NH^+$ in the reducible species favors reduction of the imine at more positive potential, the interaction between the two electron-withdrawing groups in para position has an opposite effect. Whereas the resonance interaction between two formyl groups in TPA is exceptionally strong,[9] the interactions between a carbonyl group and imino group in para position on a benzene ring are much weaker. Such weaker interaction of the carbonyl and imino group in the 1,4-position has been recently observed for the monohydrazone of TPA.[5]

The difference between the stronger interaction of two C=O groups and the weaker interaction between a C=O and a $C{=}NH^+$ group in para positions on a benzene ring is supported by a difference in reactivity in other homogeneous reactions. Whereas a strong interaction between the two CHO groups in TPA results in a higher covalent hydration,[9] no such unusual hydration has been observed with species bearing one C=O and one $C{=}NH^+$ group in para position on a benzene ring.

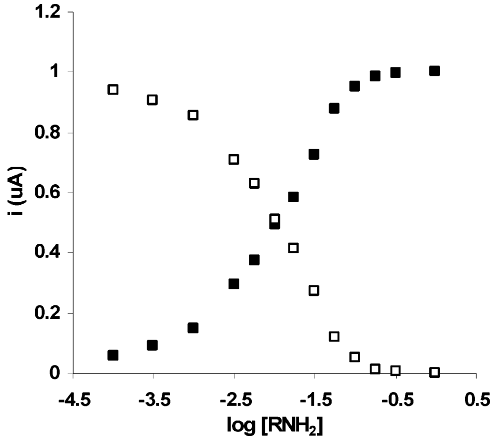
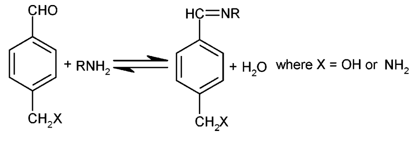


Figure 7. Comparison of the increase in wave i_2' (■) with the decrease in wave i_2 (□) with increasing concentration of 2-aminoethanol (RNH_2).

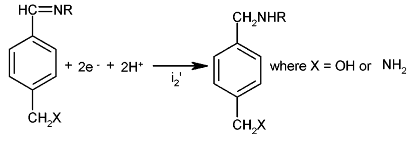
In the investigation of equilibria involving benzenoid compounds, molar absorptivities of participating species are often not accessible, and absorption bands of starting materials, intermediates, and products often overlap. In such cases, polarography sometimes offers more straightforward information. Nevertheless, because of a competition between two structural effects in the reaction of TPA with amines, in this case, the use of polarography was more limited than that of spectrophotometry, when the absorbance at 288 nm was followed. The changes of absorbances at 315 and 300 nm were less informative, as at these wavelengths all species bearing a conjugated carbonyl group contribute to the measured absorbance. The $n \rightarrow \pi^*$ transition can take place not only with parent TPA but also with all intermediates bearing a formyl group in addition to a CH=NR, CH_2OH, or CH_2NH_2 group.

From the plot of the increase of absorbance at 288 nm as a function of log [RNH_2] (Figure 5), it was possible to obtain a value of 5×10^2 L mol $^{-1}$ for K = [imine]/[dialdehyde] [RNH_2].

Polarography can, nevertheless, offer information about reactions of 2-aminoethanol with reduction products of both TPA and its imine by following the increase in wave i_2' with increasing concentration of 2-aminoethanol. The reduction of TPA (13) yields the 4-formylbenzyl alcohol that of its imine (16), the 4-formylbenzylamine. These substituted benzaldehydes can react with 2-aminoethanol (17), and the resulting imines are reduced in reaction 18.



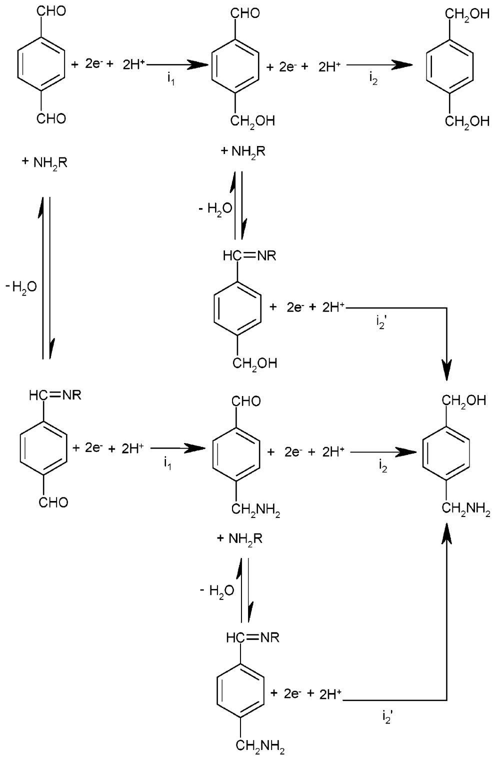
(17)



(18)

From the dependence of the limiting current due to the reduction of the imine (i_2') at pH 9.5 (Figure 6), it is possible to obtain an overall equilibrium constant K = [imine]/[all aldehydes] [RNH_2] = 0.8×10^{-2} L mol^{-1}. In this relationship, [imine] stands for the sum of concentration of imines derived from benzaldehydes substituted in 4-position by CH_2OH and CH_2NH_2 groups. Similarly, [all aldehydes] corresponds to the

SCHEME 2



sum of concentrations of the two benzaldehydes, substituted in 4-position by CH_2OH and CH_2NH_2 groups.

To express the role of the 4-CH_2NH_2 group at pH 9.5, it is necessary to consider the role of protonation at a pH close to its pK_a value. As $\sigma_{4-CH_2NH_2} = -0.11$ and $\sigma_{4-CH_2NH_3^+} = 0.29$, the average effect of the substituent at pH 9.5 can be expressed as $(\sigma_{4-CH_2NH_2} + \sigma_{4-CH_2NH_3^+})/2 = 0.08$. As the value of σ_{4-CH_2OH} is 0.01, the substituent effects of CH_2OH and CH_2NH_2 differ only slightly, and therefore the reduction potentials of both substituents are not very different. Thus, the limiting current i_2' depends on the concentration of both imines. Consequently, the plot of $i_2' = f(\log [RNH_2])$ (Figure 7) does not show any indication of two equilibria. The value of $K = 0.8 \times 10^2$ L mol^{-1} is somewhat smaller than $K = 1.4 \times 10^2$ L mol^{-1} obtained from the plot of $i_1' = f(\log [RNH_2])$ (Figure 6) for the reaction of 2-aminoethanol with 4-chlorobenzaldehyde. This is in agreement with the somewhat larger effect of the 4-Cl substituent, when compared with that of the 4-CH_2X substituent.

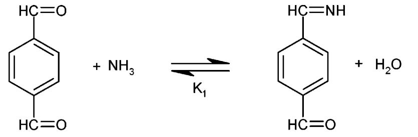
The linking of electrochemical steps (horizontal) and chemical reactions (vertical) observed for reactions of TPA with 2-aminoethanol is summarized in Scheme 2.

As in the reaction with IPA, the reaction of ammonia with TPA could be followed only at a concentration of ammonia higher than about 1.0 M, containing equal concentrations of ammonium chloride at pH 9.3. In solutions containing high concentrations of ammonium and chloride ions, the reductionof TPA takes place in two two-electron waves: i_1 at −0.86 V and i_2 at −1.23 V. The wave i_1' at −0.68 V increases with increasing concentration of ammonia (Supplemental Information 3). This wave corresponds to the reduction of the imine (20) formed in reaction 19. At the highest concentrations of ammonia, this increase is accompanied at −1.13 V by an increase of wave i_2'. This wave corresponds to a reduction (22) of the imine formed from reduction products of TPA in eq 21 and of its imine (20), formed in reaction 19:

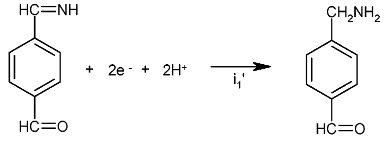
TABLE 1: Equilibrium Constants of Reactions of Aromatic Aldehydes with 2-Aminoethanol (RNH_2) and Ammonia at 25 °C

		equilibrium constant (L mol^{-1})			
compound	amine	K_1[a]	K_2[b]	n[c]	technique
IPA[c]	RNH_2	4.1×10^2		30	Pol[c]
	NH_3	2.2×10^{-1}		6	Pol[c]
		2.8×10^{-1}[d]		8	
TPA	RNH_2	6.2×10^2		11	Spec[e]
	NH_3	5.0×10^{-1}		6	Pol[c]
		4.5×10^{-1}[d]		8	Pol[c]
red-IPA[f]			1.1×10^2	13	Pol[c]
red-TPA[g]			0.9×10^2	11	
Bz4[h]			0.9×10^2	13	
4-ClBz4[i]			1.2×10^2	11	

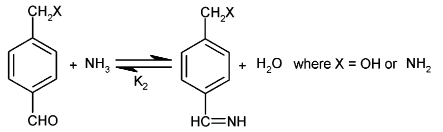
[a] K_1 = [imine]/[dialdehyde] [RNH_2]. [b] [imine]/[monoaldehyde] [RNH_2]. [c] Polarography. [d] With μ = const. [e] Spectrophotometry, λ = 288 nm. [f] Reduction products of IPA and its imine. [g] Reduction products of TPA and its imine. [h] Benzaldehyde. [i] 4-Chlorobenzaldehyde.



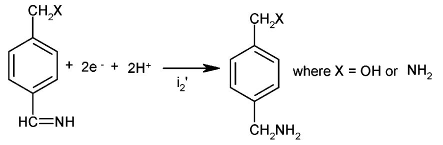
(19)



(20)



(21)



(22)

The reduction potentials of individual species are similar to that found with the imine derived from 2-aminoethanol, but are shifted to somewhat more positive potentials because of the role of the high concentration of NH_4^+ and Cl^- ions. This effect of the double layer or ion-pair formation is also responsible for the shift of the potential of the reduction of the positively charged group $C{=}NH^+$ in the reducible form of the imine to more positive potentials compared with the situation in the presence of lower concentrations of 2-aminoethanol buffers. This makes it possible from the expression $K_1 = i_1'/\ i_1\ [NH_3]$ to calculate the value of $K_1 = 0.45$. The separation of waves i_2 and i_2' was insufficient to calculate the value of K_2 in reaction 21.

Conclusions

As in acid−base equilibria, nucleophilic additions to two identical reaction centers, involving nucleophiles such as water, hydroxide ions, and nitrogen-containing nucleophiles, occur in consecutive steps rather than in a simultaneous attack. This has recently been confirmed for the reaction of TPA with hydrazine[4] and in this contribution for the reactions of both TPA and IPA with both 2-aminoethanol and ammonia.

Under conditions used, the electroreduction also occurs in two consecutive steps. This applies both for parent dialdehydes and for their monoimino derivatives. The present study demonstrates the importance of the choice of the most effective method, which even among structurally related compounds may vary. It is shown that for isomeric IPA and TPA the preference of the analytical technique used in the determination of components in equilibria may differ, depending on the nucleophile involved. Thus, for reaction of IPA with 2-aminoethanol, measurement of limiting currents in DC polarography offered a direct possibility to determine simultaneously the dialdehyde and the imine and hence to obtain the equilibrium constant. On the other hand, for the analogous reaction of the same amine with TPA, spectrophotometry was the technique of choice. For similar reaction of the dialdehydes with NH_3, polarography offered data that enabled determination of equilibrium constants for both TPA and IPA. Polarography also enabled following of condensations of reaction products containing one formyl group with 2-aminoethanol.

Comparison of equilibrium constants (Table 1) in both reactions, with 2-aminoethanol and with ammonia, shows that the reaction with TPA is shifted more in favor of the imine than the reaction with IPA. The increase in the value of K_1 for the reaction with ammonia involves a factor of about 2.0, whereas for the reaction with 2-aminoethanol, the factor is about 1.5. Taking into account that in the determination of K_1 two different techniques were used in the reaction with 2-aminoethanol, the increase in reactivity may be considered independent of the nucleophile involved.

The difference between the reactivity of both dialdehydes in the reaction with ammonia and 2-aminoethanol is striking. The increase in the value of K_1 by 3 orders of magnitude is in sharp contrast with the small change in basicity, the pK_a values of ammonia and 2-aminoethanol being about 9.3 and 9.5, respectively.

Observed changes in the reactivities in reactions of TPA and IPA reflected in values K_1 (Table 1) are in contrast with small effects of other substituents (H, 4-Cl, 4-CH_2OH, 4-CH_2NH_2, 3-CH_2OH, and 3-CH_2NH_2) on benzaldehyde on the value of the constant K_2 (Table 1). This indicates a low susceptibility of the reactions between these benzaldehydes and amines to effects of unconjugated substituents.

Supporting Information Available: Reproductions of original records of polarographic i−*E* curves and a graph, comparing the dependence of wave i_2' of TPA on concentration of 2-aminoethanol. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Roth, M. *Anal. Chem.* **1971**, *43*, 880. (b) Molnar-Perl, I. *J. Chromatogr., A* **2001**, *913*, 283. (c) Molnar-Perl, I.; Vasanits, A. *J. Chromatogr., A* **1999**, *835*, 73. (d) Zuman, P. *Chem. Rev.* **2003**, *104* (7), 3271 and references therein.

(2) Perrin, D. D.; Dempsey, B. *Buffers for pH and Metal Ion Control*; Chapman and Hall: London, 1974; p 146.

(3) (a) Zuman, P. *Collect. Czech. Chem. Commun*. **1950**, *15*, 839. (b) Zuman, P. *Nature* **1950**, *175*, 585. (c) Zuman, P. *Chem. Listy* **1951**, *45*, 65. (d) Zuman, P. *Chem. Listy* **1952**, *46*, 512, 521. (e) Zuman, P.; Brezina, M. *Chem. Listy* **1952**, *46*, 599. (f) Brezina, M.; Zuman, P. *Chem. Listy* **1953**, *47*, 975.

(4) Baymak, M. S.; Zuman, P. *Tetrahedron* **2007**, *63*, 5450.

(5) Baymak, M. S.; Zuman, P. *Tetrahedron Lett.* **2006**, *47*, 7991.

(6) Heyrovsky, J.; Kalousek, M. *Collect. Czech. Chem. Commun.* **1939**, *11*, 464.

(7) Bover, W. J.; Johnson, D.; Baymak, M. S.; Zuman, P. *Indian J. Chem. A* **2003**, *42*, 744.

(8) Baymak, M. S.; Bover, W. J.; Celik, H.; Zuman, P. *Electrochim. Acta* **2005**, *50*, 1347.

(9) Baymak, M. S.; Vercoe, K. L.; Zuman, P. *J. Phys. Chem. B* **2006**, *109*, 21928.