

Reaction of the carbonate radical with substituted anilines

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Abstract. Rate constants for the reaction of carbonate radical with aniline and some para-substituted anilines have been determined by the flash photolysis technique. Using $\sigma + \text{para}$ values the rate constants at pH 8.5 correlate very well with the Hammett equation yielding $\rho = -1$. The carbonate radical oxidises aniline giving the anilino radical. The products so formed have been identified through studies under conditions of continuous irradiation.

Keywords. Flash photolysis; carbonate radical; rate constants; substituted anilines.

1. Introduction

The carbonate radical ($E_{\text{red}}^0 = 2.1 \text{ V}$) (Endicott 1975) can react with aromatic substrates through direct electron transfer or through an electrophilic addition or substitution (Ross and Neta 1979; Chen *et al* 1975). The reaction of the carbonate radical with a series of para-substituted anilines has been examined with a view to obtain indications about the mechanism.

2. Experimental

2.1 Materials

The complex $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{ClO}_4$ is prepared according to literature procedure (Rochow 1960; Chen *et al* 1973). All the anilines were purified by recrystallisation. In the case of liquid substances, freshly-distilled samples were used for preparing solutions. For flash photolysis experiments the pH of the solutions was adjusted using KH_2PO_4 and NaOH and for continuous photolysis studies NaOH alone was used for adjusting the pH.

2.2 Measurements

Flash photolysis experiments were carried out using a 10 cm quartz cell in a Nortech flash photolysis unit type FPX-1 and the transient was recorded using data display system type DFR-2 (Nortech Laboratories, England) combined with a chart recorder (Siemens Kompensograph 111). The flash lamps dissipated up to 200 J of energy with a half peak duration of about 30 μsec . The decay of the carbonate radical was monitored by following the absorbance at 600 nm and measurement made at $23 \pm 1^\circ\text{C}$. All

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solutions were prepared with triply-distilled water and deaerated with purified N₂ before flashing. However, it was found that dissolved oxygen has no effect on the kinetic data. Only freshly-prepared solutions were used for flash photolysis studies to exclude possible thermal reaction and were discarded after a single flash.

2.3 Product analysis

Product analysis studies were carried out by continuous photolysis with a 48 W low pressure Hg vapour lamp (Rayonet RUL 2537 A). Before the carbonatotetramine-cobalt(III) salt is used as a source of carbonate radical for continuous irradiation studies, experiments were conducted leaving the reaction mixture in the dark and it was noticed that in dark this Co(III) complex oxidises aniline slowly. In order to further minimise their reaction, the solution is well cooled and the complex salt is added at the last moment before irradiation. After irradiation the products are immediately extracted with ether. In a typical experiment, a solution containing 10⁻² M complex and 10⁻³ M aniline at pH 8.5 is irradiated for 30 min after deaeration with purified N₂ or Ar. The residue from the ether extract is separated and identified by TLC. 4-aminodiphenylamine, azobenzene and benzidine are the major products and 2-aminodiphenylamine and hydrazobenzene are formed in trace amounts. In addition, phenylhydroxylamine is also formed. Azobenzene is formed by the rapid oxidation of hydrazobenzene. Therefore in these experiments azobenzene was identified as a major product and hydrazobenzene as a minor product. UV spectrum of these separated products compared well with that of authentic samples. The separated amines are also mixed with *p*-dimethylaminobenzaldehyde and the visible spectra of the resulting derivatives (Zechner *et al* 1976) compared well with those of authentic samples. Under these conditions aniline itself without added complex underwent photolysis yielding the same products, except phenylhydroxylamine, but in considerably reduced yields. In mixtures the Co(III) complex is the major absorber of the radiation and not aniline. At 254 nm, the extinction coefficients for cobalt(III) complex and aniline are found to be 11340 and 669 M⁻¹ cm⁻¹ respectively. In the dark the complex plus aniline gets slowly oxidised at 40°C to give phenylhydroxylamine and the products such as 4-aminodiphenylamine, hydrazobenzene, etc which were isolated in photolytic conditions were conspicuously absent. These results show that the greater yield of 4-aminodiphenylamine, azobenzene, benzidine and 2-aminodiphenylamine that are obtained on irradiating the carbonatotetraminecobalt(III) complex with aniline result from the reaction of the carbonate radical with aniline.

3. Results

The carbonate ion radical is produced on flashing a solution containing about 2 × 10⁻⁵ M [Co(NH₃)₄CO₃]ClO₄ by charge transfer to metal (CTTM) transition (Cope and Hoffman 1972; Chen *et al* 1973).



The carbonate ion radical CO₃⁻ and its conjugate acid, the bicarbonate radical CO₃H⁻ (pK_a = 9.6 ± 0.3) (Cope and Hoffman 1972; Chen *et al* 1973) have identical spectra with λ_{max} equal to 600 nm and the rate was followed by observing the absorbance at this

wavelength. The flash output energy and the concentration of the complex were so adjusted as to produce initially 1.5×10^{-6} M carbonate radical. The decay is second order in the absence of any scavenger (decay constant $2 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$) and becomes pseudo-first order in the presence of added scavenger. This pseudo-first order rate constant is determined at least three different initial concentrations of scavenger and at each concentration at least four kinetic curves were processed. Second order rate constants were determined from the slope of the plots of the pseudo-first order rate constants vs [scavenger] (figure 1). The rate constants obtained for aniline and some parasubstituted anilines at pH 8.5 are given in table 1. These data are subject to an error inherent in flash photolysis studies ($\pm 10\%$).

The effect of pH on the rate constant for the reaction of carbonate ion radical with aniline is studied. The rate constant remains almost constant in the pH range 6–11.

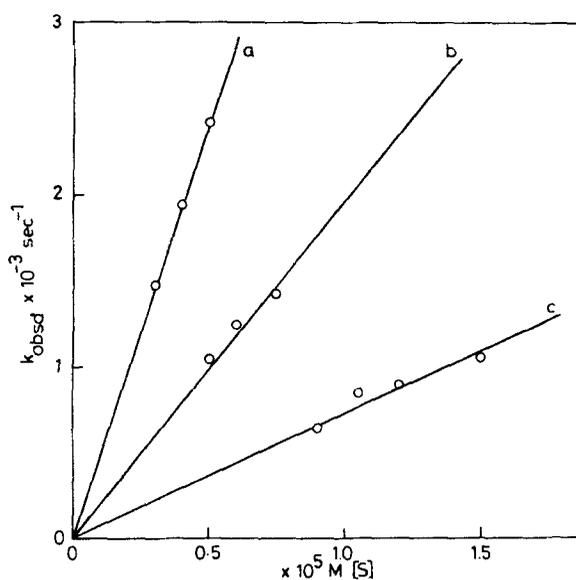


Figure 1. Dependence of k_{obs} on scavenger concentration at pH = 8.5, a. aniline b. *p*-aminobenzoic acid c. *p*-nitroaniline.

Table 1. Rate constants for the reaction of $\text{CO}_3\text{H}^\cdot$ with aniline and *p*-substituted anilines (pH = 8.5).

Scavenger	$k_2 \text{ M}^{-1} \text{ sec}^{-1}$
Aniline	5.0×10^8
<i>p</i> -chloroaniline	4.3×10^8
<i>p</i> -bromoaniline	3.8×10^8
<i>p</i> -aminobenzoic acid	2.0×10^8
<i>p</i> -aminoethylbenzoate	2.0×10^8
<i>p</i> -nitroaniline	7.3×10^7
<i>p</i> -fluoroaniline	6.2×10^8
<i>p</i> -toluidine	9.1×10^8

Since the pK_a of aniline is 4.63, it remains in the basic form throughout the pH range studied and only the bicarbonate radical deprotonates between pH 9 and 10. The pH independence of the rate constant shows that the intrinsic reactivity of CO_3H^\cdot and $CO_3^{\cdot-}$ towards aniline is the same.

4. Discussion

To understand the effect of substituent on the reactivity of aniline with carbonate radical the rate constants given in table 1 are correlated with appropriate Hammett substitution constants. With σ_p^+ values (Brown and Okamoto 1958) a good correlation is obtained (figure 2). The ρ value of -1 obtained is similar to that observed for the reaction of carbonate ion radical with substituted phenols (Moore *et al* 1977). Crable and Kearns (1962) found that the ionization potentials of the *p*-substituted anilines correlate well with σ_p^+ values. Thus it is possible that the rate constants are influenced by the ionization potentials of the amine suggesting possible electron transfer from aniline to the carbonate radical. Attempts were therefore made to observe the possible anilino-radical intermediate. Since the pK_a of the anilino radical $C_6H_5NH_2^{\cdot+}$ is 7 (Land and Porter 1963), at pH 8.5 it deprotonates to give $C_6H_5NH^\cdot$. For the protonated and basic forms of the anilino radical, absorption maxima of 423 and 300 nm respectively have been reported by Land and Porter (1963). When a solution containing 3×10^{-5} M $[CO(NH_3)_4CO_3]ClO_4$ and 2×10^{-5} M aniline at pH 8.5 is flashed with about 125 J of energy there is very little absorption in the 423 nm region and the absorption around 300 nm could not be followed due to limitations of

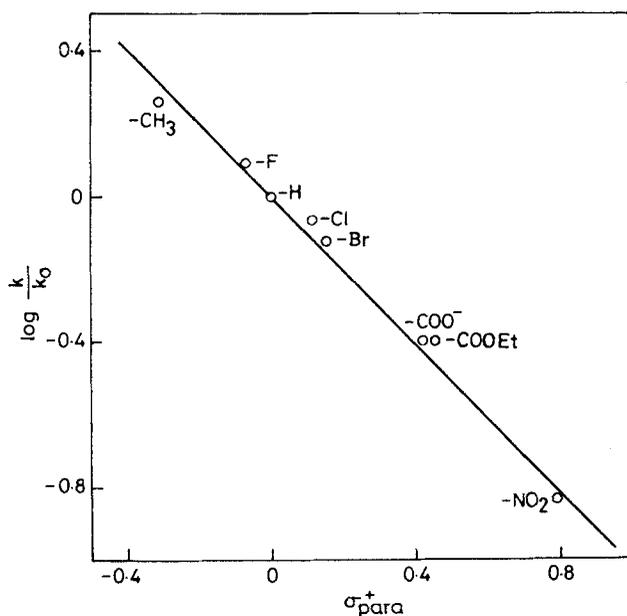


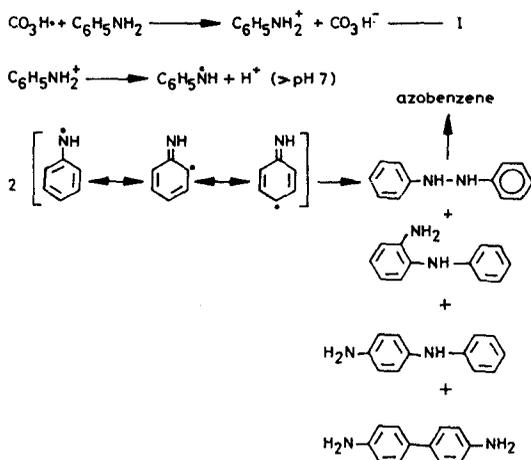
Figure 2. Hammett plot for the reaction of CO_3H^\cdot radical with substituted anilines at pH 8.5.

the monitoring source. But on flashing the same solution with the same energy at pH 6 a transient absorption around 424 nm was observed at 1 msec after the start of the flash. This transient absorption was identical with that reported (Land and Porter 1963; Christensen 1972) for $C_6H_5NH_2^+$. In the absence of the $[Co(NH_3)_4CO_3]ClO_4$ complex, aniline failed to give detectable absorption in this region, probably because of the smaller flash energy. Since the pK_a value of the bicarbonate radical is 9.6 ± 0.3 at both pH 6 and 8.5 the bicarbonate radical will exist mainly in the protonated form CO_3H^\cdot . Hence at pH 8.5 also the formation of $C_6H_5NH_2^+$ is expected but will immediately deprotonate to give $C_6H_5NH^\cdot$ which dimerises to give hydrazobenzene and other observed products (scheme 1).

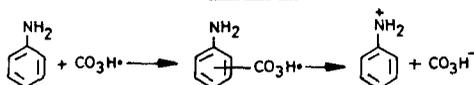
Though the σ_p^+ values correlate very well with $\log k$ of substituted aniline, figure 2 cannot be taken as a definite indication of the mechanism of the reaction, *i.e.* electron transfer or radical attachment. The $\rho\sigma_p^+$ correlation has also been applied to electrophilic aromatic substitution (Exner 1972) and step 1 of scheme 1 may involve the intermediacy of an adduct (scheme 2).

The adduct could rearrange by an overall electron transfer mechanism to give the anilino radical. Since no specific transient other than anilino radical could be observed in the region 350–650 nm, the formation and collapse of the adduct may be very rapid and these two processes may be completed before any observation could be made. It is believed that such an adduct may indeed exist since a similar reactivity for both the forms of the radical towards aniline has been observed. If a direct electron transfer mechanism were operating, then one would expect the uncharged protonated form CO_3H^\cdot to be a stronger oxidising agent and thus to react more rapidly in an electron transfer process than $CO_3^{\cdot-}$. However both forms could show similar reactivity if H abstraction or addition modes were operative.

SCHEME - 1



SCHEME - 2



It would be interesting to compare the reaction of OH[·] radical (Christensen 1972) and aniline with that of carbonate radical. The highly reactive OH[·] radical reacts with aniline to give both cyclohexadienyl type radical and anilino radical. The less reactive CO₃H[·] radical is more selective and gives only anilino radical.

The reaction of carbonate radical with aliphatic amines is also studied and the rate constants are found to be two or three orders lower than those for aniline. These rate constants do not give a satisfactory correlation with their ionization potentials. With amines like RCH₂NH₂ products like RCHO are identified, probably formed by α-hydrogen abstraction. Detailed studies of these systems are in progress.

5. Conclusion

It may be concluded that carbonate radical oxidises aniline to anilino radical. Anilines containing electron donating *p*-substituents have higher rate constants at pH 8.5 compared to unsubstituted aniline whereas the converse is observed for anilines containing electron withdrawing *p*-substituents.

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