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REACTIONS OF THE CARBONATE RADICAL WITH ALIPHATIC AMINES

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Abstract - Carbonate radicals react with aliphatic amines by a dual mechanism, viz. (i) hydrogen abstraction and (ii) electron transfer. The former is more probable with primary amines. Tertiary amines react via electron transfer. Both mechanisms may operate in secondary amines. Cyclic tertiary amines react with different rates and their relative reactivities are explained on the basis of the concept of Hoffmann's 'through bond' interaction.

Introduction:

Oxidation of amines can be effected by a variety of chemical one electron oxidants, electrochemically, photochemically and enzymatically[1,2]. Another pathway for the oxidation of amines which has not received much attention is their reaction with oxidising free radicals. Carbonate radical $CO_3^{\bar{\cdot}}$ has been shown to be a good one electron oxidant ($E^{o}_{red} = -2.1$ V) and there are reports[3a,3b] on the mode of attack of this radical on aromatic amines. In the present paper the reaction of this radical with a number of aliphatic amines is discussed.

Results and Discussion:

The carbonate radicals are produced by the flash photolysis of deaerated solutions containing about 1 mM $K_2S_2O_8$ and 0.2M Na_2CO_3. The sulphate radicals produced by the photolysis of $S_2O_8^{2-}$ ions oxidise the carbonate ions to radicals very efficiently[4,5]. A high concentration of Na_2CO_3 ensured fast and efficient

$$S_2O_8^{2-} + h\nu \longrightarrow 2\ SO_4^{\bar{\cdot}}$$

$$SO_4^{\bar{\cdot}} + CO_3^{2-} \longrightarrow SO_4^{2-} + CO_3^{\bar{\cdot}}$$

conversion of CO_3^{2-} to $CO_3^{\bar{\cdot}}$ and precluded the competitive reaction of sulphate radicals with organic substrates present in the solution. Further, some experiments were also carried out by using $[Co(NH_3)_4CO_3]ClO_4$ as a source of carbonate radicals[17] for comparison. No difference was noted.

$$[Co(NH_3)_4CO_3]^+ + h\nu \xrightarrow{\underline{CTTM}} Co^{2+} + 4\ NH_3 + CO_3^{\bar{\cdot}}$$

The absorption of the carbonate radical at 600 nm ($\varepsilon = 1830\ M^{-1}cm^{-1}$)[17] was observed immediately after the light pulse. The decay of the radical is second order in the absence of any scavenger (decay constant 2 x 10^7 $M^{-1}s^{-1}$) and becomes pseudo-first order in the presence of added amine. The pseudo-first order rate constants (k') were determined for at least three different initial concentrations of scavenger and at each concentration at least three kinetic curves were processed. From the plot of k' vs [Amine] the second order rate constants for the reaction of carbonate radical with amines were derived. The rate constants (k) obtained for a number of primary, secondary and tertiary amines at pH 11.5 are given in Table 1. The data are subject to the errors inherent in flash photolysis studies.

Table 1. Rate constants for the reaction of $CO_3^{\bar{\cdot}}$ radicals with aliphatic amines, pH = 11.5

Amine	k $M^{-1}s^{-1}$
n-Butylamine	4.0 x 10^5
Isobutylamine	4.0 x 10^5
t-Butylamine	5.8 x 10^4
Cyclohexylamine	7.2 x 10^5
Isopropylamine	5.0 x 10^5
Benzylamine	7.5 x 10^5
Diethylamine	3.8 x 10^6
Di-n-propylamine	4.5 x 10^6
Di-n-butylamine	5.0 x 10^6
Piperidine	3.3 x 10^6
Triethylamine	6.4 x 10^6
1,4-Diazabicyclo[2.2.2]octane	1.7 x 10^{7*}
Hexamethylenetetramine	1.7 x 10^4
N,N-Dimethylbenzylamine	3.4 x 10^6
N-methylpiperidine	2.6 x 10^6
N,N-Dimethyl t-butylamine	3.0 x 10^6

*Monitoring wavelength 620 nm.

Two possible mechanisms for the oxidation of amines by one electron oxidants involve (i) direct-electron transfer and (ii) H-atom abstraction as the rate determining steps[1]. Scheme I explains these two modes of attack of the $CO_3^{\bar{\cdot}}$ radical on the amines. The bond dissociation energy for N-H (cited for CH_3NH_2) is approximately 103 kcal as compared to about 75 kcal for benzylic hydrogen and 94 kcal for α-hydrogen in CH_3NH_2. Therefore H abstraction from the nitrogen atom should be a generally less favourable mode of attack. This assumption of α-hydrogen abstraction is also in accordance with the observed low reactivity of t-butylamine which lacks an α-hydrogen atom.

Both the mechanisms indicate the eventual formation of the same amino alkyl radical ($R\dot{C}HNR_2'$ or $R\dot{C}HNH_2$). In the electron transfer mechanism this radical is formed by the deprotonation[6] of aminium cation radical (eqn. 2 in Scheme I). The aminoalkyl radical is a strong reducing agent[6] and readily undergoes oxidation to the imine in the presence of mild oxidants present in the solution (eqns. 3 and 7). Two aminoalkyl radicals can couple[7] to give an imine (eqn. 6). The imine produced is readily hydrolysed in the presence of alkali to yield the carbonyl compound as the end product. The reaction products identified with some amines are given in Table 2.

SCHEME I

(i) Direct one electron transfer:

$$RCH_2\dot{N}R'_2 + CO_3^{\cdot-} \longrightarrow RCH_2\overset{\cdot+}{N}R'_2 + CO_3^{2-} \qquad (1)$$

$$RCH_2\overset{\cdot+}{N}R'_2 \xrightarrow{-H^+} R\dot{C}HNR'_2 \qquad (2)$$

$$R\dot{C}HNR'_2 \xrightarrow{ox} RCH{=}\overset{+}{N}R'_2 \qquad (3)$$

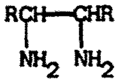
$$RCH{=}\overset{+}{N}R'_2 \xrightarrow{OH^-/H_2O} RCHO + HNR'_2 \qquad (4)$$

(ii) α-Hydrogen abstraction:

$$RCH_2NH_2 + CO_3^{\cdot-} \longrightarrow R\dot{C}HNH_2 + CO_3H^- \qquad (5)$$

$$2\ R\dot{C}HNH_2 \longrightarrow RCH{=}NH + RCH_2NH_2 \qquad (6)$$

$$2\ R\dot{C}HNH_2 \longrightarrow$$



$$RCH(NH_2){-}CH(NH_2)R$$

Or

$$R\dot{C}HNH_2 \xrightarrow{ox} RCH{=}NH \qquad (7)$$

$$RCH{=}NH \xrightarrow{OH^-/H_2O} RCHO + NH_3 \qquad (8)$$

Table 2. Products identified in the reaction of $CO_3^{\cdot-}$ radical with some aliphatic amines

Amine	Product identified	Method
n-Butylamine	n-Butyraldehyde	by glc and as 2,4-dinitrophenylhydrazone derivative
Cyclohexylamine	Cyclohexanone	-do-
Di-n-propylamine	n-Propionaldehyde	as 2,4-dinitrophenylhydrazone derivative
Triethylamine	Acetaldehyde	-do-

Although the order ter > sec > pri is expected for both mechanisms, the reactivity gradient would be smaller if a H abstraction mechanism was operating[8]. It is evident from Table 1 that the amines show only a small reactivity gradient and this is in favour of the H abstraction mode. Thus, from the order of reactivity or from the product analysis it is not possible to unequivocally decide whether the mechanism is an electron transfer or a H abstraction. Further, the intermediates, the alkylaminium cation radical and the amino alkyl radical formed in the electron transfer and H abstraction mode respectively, are highly unstable and direct observation of these radicals is difficult. However, in the case of the aromatic amines the available data indicate that carbonate radical reacts with the amine by an electron transfer mechanism[3a]. Here again, the electron transfer is succeeded by the formation of an adduct. Since aliphatic amines behave differently from aromatic amines it would be interesting to study the reactivities of cyclic amines also. Cyclic amines are expected to exhibit some properties characteristic of aliphatic tertiary amines although by virtue of their rigid geometric structures they would show some differences from the open chain amines. Thus in this context, some tertiary amines like 1,4-diazabicyclo[2-2-2]octane (DABCO) and 1,3,6,8-tetraazatricyclo[4.4.1.1]dodecane (TATCD) which were shown to give somewhat stable aminium radicals in cyclic voltammetric studies[9] as well as hexamethylenetetramine (HMT) were chosen and their reaction with carbonate radical studied.

The transient spectra obtained in the reaction of DABCO and TATCD with $CO_3^{\cdot-}$ were recorded. The transient with λ_{max} 465 nm observed in the case of DABCO is found to be idential to that reported for $DABCO^{+}$ cation radical by Ernstbrunner et al.[10]. This clearly demonstrates the electron transfer from the nitrogen of DABCO to $CO_3^{\cdot-}$ radical.

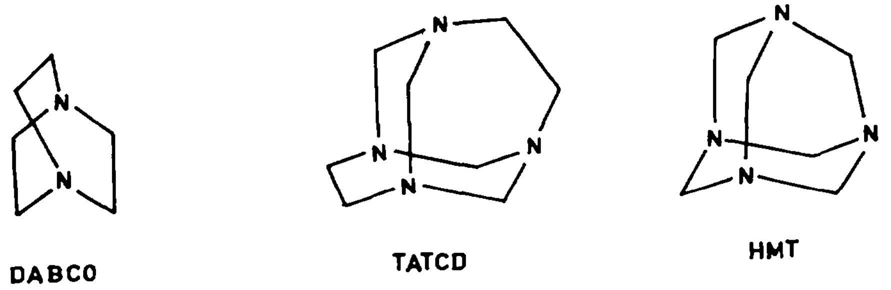


FIG. 1

The other cyclic tertiary amine, TATCD which is structurally similar to DABCO is also found to be quite reactive towards carbonate radical and produces a transient centred at 570 nm, stable over several milliseconds. In analogy with DABCO, this transient absorption at 570 nm is attributed to $TATCD^{+}$ cation radical based on its stability, inertness towards oxygen and absorption in the visible region. This assignment is corroborated by the observation of other workers. Nelson and Buschek[11] have obtained a dark purple coloured transient (spectrum not reported) at -100°C during the oxidation of TATCD by tris-(p-bromophenyl)ammonium hexachloro antimonate in butyronitrile. Cyclic voltammetric studies of TATCD at gold electrode in acetonitrile by Nelson and Hintz[9] have revealed that $TATCD^{+}$ cation radical was stable enough to give a rereduction wave.

Our observations regarding the stability of these cation radicals are in good agreement with the conclusions of other workers[10,11]. The extra stability of these radicals is due to the operation of the 'through-bond and through-space' interactions in these systems. These systems serve as good models for testing the concepts of Hoffmann[12].

Hexamethylenetetramine (HMT) was relatively inert. The reactivities of the cyclic amines are in the order TATCD $\sim$ DABCO >> HMT. HMT is thousand times less reactive than the other two. Further, HMT does not yield its cation radical under these flash photolytic conditions. All these observations are to be expected on the basis of Hoffmann's theory. DABCO and TATCD possess C-C bonds parallel to N-N lone pair orbitals favouring a strong 'through-bond interaction' between N-N lone pair orbitals and σ and σ^* orbitals of C-C. These interactions lower the ionisation potentials and stabilise the cation radicals. In the case of HMT such a parallel alignment and consequent 'through-bond interaction' is not possible.

The identification of $DABCO^+$ and $TATCD^+$ radical intermediates definitely establishes electron transfer from amine to carbonate radical in these cyclic amines. A good correlation is obtained in the case of all tertiary amines, cyclic as well as open chain amines, when log k values are plotted against the oxidation peak potentials, E_p^{ox} (Fig. 2; E_p^{ox} values taken from refs. 9,13). Such a linear relationship between log k and E_p^{ox} has also been obtained for the one electron oxidation of tertiary amines by alkaline hexacyanoferrate(III) ions[13]. This kind of linear correlation suggests that the oxidation of all tertiary amines by carbonate radical takes place through electron transfer.

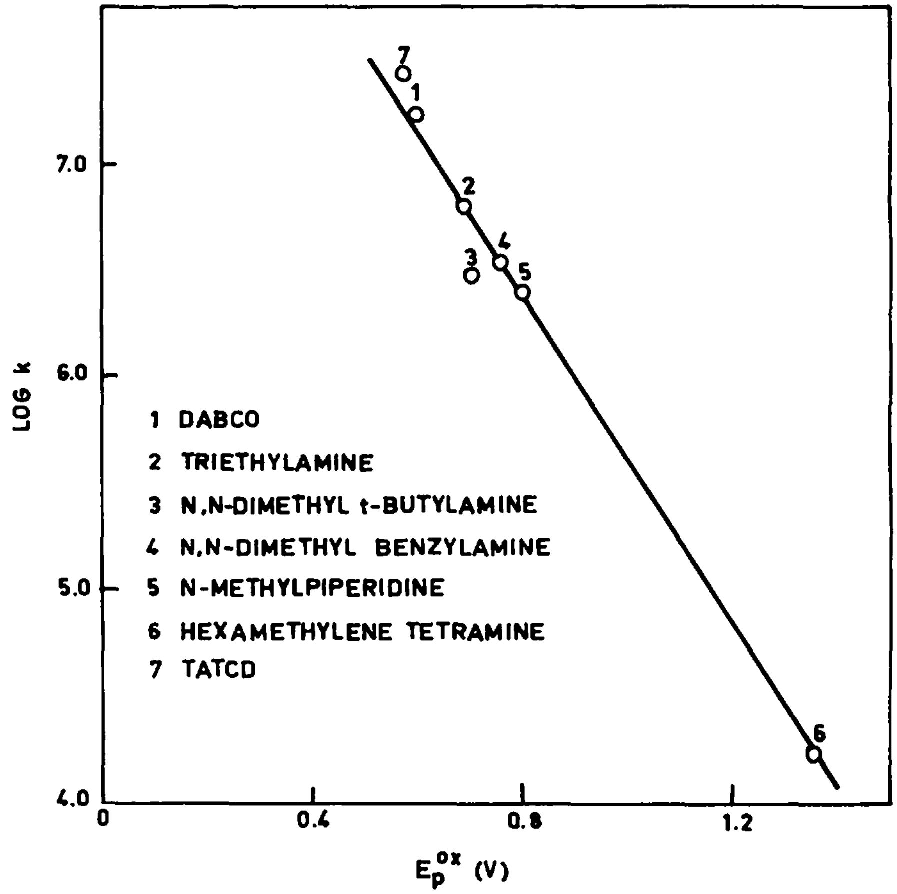


FIG. 2 PLOT OF LOG k Vs OXIDATION PEAK POTENCIALS OF SOME TERTIARY AMINES

If the mode of attack by $CO_3^{\cdot-}$ is simply removal of an electron from the orbital localised on nitrogen atom, then the effect of change in the molecular structure on the rate should be determined largely by inductive effects. In such a case the plot of logarithm of rate constants versus σ^* Taft substitution constants would afford a linear relationship[14]. The carbonate radical failed to give such a correlation for the amines studied. This rules out the possibility of electron transfer being the only mechanism operating in all the pri-, sec- and ter-amines. Further, if direct electron transfer mechanism was operating then a greater reactivity gradient is expected on passing from pri- to ter-amines because of the direct inductive effect of the alkyl groups. As already pointed out this is not observed. The tertiary amines are only slightly more reactive than the secondary amines and in some cases the secondary amines are equally reactive. Thus, these data indicate a H abstraction mechanism for all the amines except tertiary amines. In cyclic amines like DABCO, because of the restricted rotation of the C-N bond, the conformational requirement for a facile α-C-H bond breaking is not met and it is expected to be less reactive than acyclic tertiary amines like Et_3N[15].

All the results can be explained in terms of the dual mechanism concept. The linearity of the plot of log k vs E_p^{ox} in the case of the tertiary amines shows that the favoured mechanism for tertiary amines is electron abstraction. In the case of cyclic tertiary amines like DABCO and TATCD which possess characteristic geometric structures the corresponding cation radicals are stable and can be detected. Primary amines react mainly by α-hydrogen abstraction. With secondary amines electron transfer and hydrogen abstraction may be competitive or both may operate, one being a more dominant process.

EXPERIMENTAL

All chemicals used in this investigation were of analytical grade. The complex $[Co(NH_3)_4CO_3]ClO_4$ was prepared according to the procedure in the literature[16,17]. Freshly distilled samples of amines were used for preparing the solutions. In the case of some solid amines recrystallised samples with correct melting points were used.

Flash photolysis experiments were carried out in a Nortech Flash Photolysis apparatus described previously[3]. The half width of the flash duration was determined to be about 30 μs. The decay of the carbonate radical was monitored by following the absorbance at 600 nm and measurements made at 23 ± 1°C. The concentrations employed were as follows: $CO_3^{\overline{\cdot}}$: $\sim 10^{-6}$M; amines: 10^{-6} to 10^{-4}M. Continuous photolysis experiments were carried out with 48 W low pressure Hg lamps (Rayonet RUL 2537 Å).

All solutions were prepared with triply distilled water and deaerated with purified nitrogen before flashing. Only freshly prepared solutions were used in order to exclude possible thermal reaction and were discarded after a single flash.

Product analysis:

Continuous irradiation experiments were carried out to identify the end products and in a typical experiment a well cooled deaerated aqueous solution containing 1 mM $K_2S_2O_8$, 0.3M Na_2CO_3 and about 0.5 mM of amine was irradiated in a quartz tube with 254 nm light for about 20 minutes. Unless catalysed by ions like Ag^+ the thermal oxidation of aliphatic amines by persulphate is quite slow and is of no consequence[18,19]. Immediately after irradiation, the organic materials were extracted from the alkaline mixture into ether. The ether solution was dried over anhydrous $MgSO_4$, evaporated to a small volume and analysed by GLC. As an alternative method, 2,4-dinitrophenylhydrazine reagent was added to the ether extract and the phenylhydrazones formed were identified by TLC and separated from the excess 2,4-dinitrophenylhydrazine by column chromatography. The IR spectra of the 2,4-dinitrophenylhydrazones compared well with those of the authentic samples.

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