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RADIOLYSIS OF AQUEOUS SOLUTIONS OF AMMONIUM BICARBONATE OVER A LARGE DOSE RANGE

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Abstract. O₂-free aqueous solutions of 0.05 mol dm⁻³ ammonium bicarbonate were studied after receiving various doses of ⁶⁰Co gammas (0.001-170 Mrd) or krd pulses of 10 MeV electrons. Formate, oxalate, formaldehyde and an unidentified polymer (M_w14000-16000 daltons) were found to be the main radiolytic products. A large initial yield of formate in the γ-radiolysis, G(HCOO⁻) = 2.2, is due to the reaction CO₂⁻ + HCO₃⁻ ⇌ HCOO⁻ + CO₃⁻. The efficiency of organic synthesis within the large dose range studied is low and is explained by efficient pathways to the reformation of bicarbonate, where the reaction CO₂⁻ + CO₃⁻ is particularly significant. Computer fitting of the data obtained in the γ-radiolysis and by pulsed electron beam experiments gives k(CO₂⁻ + HCO₃⁻) = (2 ± 0.4) × 10³ dm³mol⁻¹s⁻¹, k(CO₂⁻ + CO₃⁻) = (5 ± 1) × 10⁷ dm³mol⁻¹s⁻¹, k(NH₂ + HCO₃⁻) < 10⁴ dm³mol⁻¹s⁻¹ and k(NH₂ + CO₃⁻) = (1.5 ± 0.5) × 10⁹ dm³mol⁻¹s⁻¹.

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1. INTRODUCTION

Bicarbonate was examined as the carbon source for radiation-induced synthesis of simple organic compounds in experiments relevant to economic fixation of carbon^(1,2) or to the origin of biologically significant compounds on the primitive earth⁽³⁾. The data presently available are not sufficient to explain the radiolytic behaviour of the bicarbonate solutions in spite of the well-established behaviour of the carbonate radical-ion^(4,5,6). Such an understanding is needed, however, also in studies where bicarbonate is not initially present in the system but does accumulate with dose as a result of decomposition of its constituents. In some cases ^(7,8) the accumulated bicarbonate may become even one of the dominant constituents at advanced stages of radiolysis.

2. EXPERIMENTAL

2.1. Samples

The syringe technique and bubbling with argon were used in preparing fresh, O₂-free, samples for each irradiation. When larger amounts of the sample were needed for analysis a Pyrex vessel (450 ml) was used. The vessel was provided with a cap that permitted radiolytically produced H₂ at larger doses to diffuse out gradually to avoid build-up of an overpressure above the liquid, and to prevent air from entering the solution. Ammonium bicarbonate, sodium bicarbonate, ammonium carbonate and ammonium carbamate were Merck products (highest purity available).

2.2. Irradiation

⁶⁰Co gammas at a dose rate of 1.3 Mrd h⁻¹ were delivered in a 50 kCi (nominal) irradiation unit at CEN-UNAM (Mexico), at sample temperatures up to 40°C.

In pulsed electron beam experiments the 10-MeV HRC accelerator at Risø was used with a pulse width of 0.2 μ s and a dose of 0.05-2.0 krd. The optical detection system consists of a 150-W Varian high-pressure xenon lamp and a Perkin-Elmer double quartz prism monochromator with a 1P28 photomultiplier. The data were recorded on a Nicolet Explorer III digital storage oscilloscope and stored on disks. The data treatment was performed by using an on-line PDP-8 computer.

2.3. Analyses

Reduction of Ce^{4+} in acid medium was used for the determination of formic acid. All simple organic compounds apart from formic acid are oxidized in 4 M persulfuric acid. The difference of ceric ion concentrations in H_2SO_4 (concentrated) and $HClO_4$ (4 M) was obtained from spectrophotometric measurements at 320 nm and used in calculating of the $HCOOH$ concentration. Low concentrations of H_2O_2 do not affect the finding on formic acid under our conditions. Some complementary measurements were also made with chromotropic acid.

A search for aldehydes, carboxylic acids, hydrazine and hydroxylamine was made by introducing an aliquot irradiated sample directly into the gas chromatograph, a Varian Aerograph 2400 instrument with a Hewlett-Packard integrator terminal 3388A and a flame ionization detector; the stainless steel column was packed with the Chromosorb 102. During a run the temperature rose from 60°C to 230°C at increments of 6°C min^{-1} . The detection limits were 10^{-6} mol dm^{-3} or lower⁽⁹⁾.

Another search for aldehydes and keto acids was made after the separation with 2,4-dinitrophenylhydrazine: it was performed by paper chromatography or a subsequent esterification and gas chromatography.

Formaldehyde was measured by spectrophotometry with 2,4 dinitrophenylhydrazine at $\lambda = 432$ nm and $\epsilon_{432} = 14667$ mol $^{-1}$ cm $^{-1}$. The method was considered satisfactory since the search for aldehydes and keto acids has shown only the presence of formaldehyde.

The nonvolatile radiolytic products were concentrated by evaporating the irradiated solution at reduced pressure and 45°C; the undecomposed bicarbonate was eliminated by subsequent heating at 50°C for 20-30 minutes.

Oxalic acid was determined by gas chromatography from the dry residue by using a procedure for esterification and separation given elsewhere⁽¹⁰⁾.

A search for glycine was made by spectrophotometry with ninhydrin or by gas chromatography of volatile derivatives.

A molecular weight determination was made with a HPLC (Varian 5000) on the Micro Pak TKS Gel 2000 SW column (30x0.75 cm), using sodium phosphate buffer (pH 7) as eluent⁽⁸⁾.

Routine KBR technique and a Perkin Elmer 599B instrument were used for recording the IR spectra. Blanks were treated in the same way as the irradiated samples.

3. COMPUTER SIMULATION

The reaction mechanism and the formation of products were analysed by computer simulation using the CHEMSIMUL program⁽¹⁰⁾ on a Burroughs 7800 computer.

The following main bimolecular reactions of primary water radicals were included in the reaction scheme which usually consisted of about one hundred reactions:

If not otherwise stated, the rate constants are taken from refs. 11 and 12. The values of $G_{e_{\text{aq}}^-}$, G_{H} and G_{OH} were taken from ref. 13.

4. RESULTS AND DISCUSSION

4.1. General

Throughout the dose-range used the radiolytic products were formate and oxalate and an unidentified polymer (M_w 14000-16000 daltons) (Fig. 1), besides H_2 from water decomposition and trace amounts of formaldehyde and H_2O_2 . A search for other products like CO, $(\text{CHC})_2$, CH_3CHO , CHOCOO^- , NH_2NH_2 , NH_2OH and $\text{NH}_2\text{CH}_2\text{COO}^-$ gave negative answers with methods which had detection limits of $10^{-6} \text{ mol dm}^{-3}$ or lower.

By dissolving $5 \times 10^{-2} \text{ mol dm}^{-3}$ ammonium bicarbonate in water the pH of the solutions becomes 7.8. Besides the bicarbonate ion, the solution contains equilibrium concentrations of carbon dioxide and carbonate:

Because of the presence of ammonia, one has also to consider the equilibrium

When the pH effect was examined (pH between 6 and 12), ammonia, sodium hydroxide, and ammonium or sodium carbonate were used. The solutions contained also some carbamate in equilibrium with carbonate when prepared from ammonium carbonate, but only micromol amounts since the equilibrium in dilute solutions shifts strongly towards bicarbonate(14).

Reactions of the solutes used in this work with the primary radicals in water are well established; the following reactions are significant under our working conditions:

4.2. Formate and oxalate

The formation of formate (Fig. 1A) occurs in a large initial yield, $G^0(\text{HCOO}^-) = 2.2$, while that of oxalate (Fig. 1B), $G^0(\text{C}_2\text{O}_4^{2-}) = 0.05$, is lower than expected from the known reactions of carboxyl radical-ion $\text{CO}_2^{\cdot -}$

Therefore we have examined the kinetic behavior of the $\text{CO}_2^{\cdot -}$ radical ion in aqueous (O_2 -free) solutions containing various concentrations of sodium bicarbonate ($0.025 - 1 \text{ mol dm}^{-3}$). The bimolecular second order decay of $\text{CO}_2^{\cdot -}$ (reaction (13)) measured at $\lambda = 250 \text{ nm}$ is dominant in dilute solutions at larger doses per pulse, and the second-order rate constant is in agreement with literature values(16). This supports the larger yields of oxalate ($G = 0.4-1.7$) which were reported in the earlier work(1) with 2-MeV electrons, where 0.1-1% solutions of ammonium, sodium or calcium bicarbonate were irradiated. However, at low doses per pulse (50 rd) and larger concentrations of bicarbonate ($0.5-1 \text{ mol dm}^{-3}$) mixed kinetics of the $\text{CO}_2^{\cdot -}$ radical-ion decay are observed. The presence of a pseudo-first-order process at the end of the decay indicates a reaction of the carboxyl radical-ion with the solute.

A minor loss of carboxyl radicals is attributed to the cross reaction between the CO_2^- and CO_3^-

The values k_{15} and k_{16} were derived by computer fitting of the experimental data on the initial yields of formate and oxalate in γ -radiolysis, and on the dependence of transient absorbancy on the dose per pulse and the bicarbonate concentrations (up to 1 M). The reaction scheme also include the following reactions:

A comparison of calculated and measured data suggests that the eqs. (1-20) given above, as well as those relevant to ammonia (eqs. 21-23), can account for the formation yields of formate and oxalate. The formation of oxalate by reaction (13) occurs in competition with reactions (14)-(16). The reactions (15) and (20) are equilibrium reactions. These are efficient only at low dose rates and larger bicarbonate concentrations and explain the high initial yield of formate in γ -radiolysis. As a consequence, the recombination of carboxyl radical-ions (eq. 13) decreases and explains the low yields of oxalate found presently with ^{60}Co gamma rays, and previously⁽²⁾ with suspensions of various metal carbonates which were irradiated with 70 keV X-rays or gammas from radioactive cobalt.

At larger doses the formate and oxalate appear in low steady-state concentrations, about 2×10^{-6} and $6 \times 10^{-5} \text{ mol dm}^{-3}$ respectively (Figs. 1A and B). The accumulation of primary and secondary radiolytic products, particularly formaldehyde and polymeric material, complicates the reaction scheme, and computer simulations cannot be done with existing experimental data.

4.3 Formaldehyde

Formaldehyde is present in concentrations lower by one order of magnitude than formic acid. The steady-state concentration (2×10^{-7} mol dm⁻³) starts after about 5 krd, and the dosage curve suggests that it is a secondary product from the radiolytic decomposition of formate.

4.4. Polymeric material

The dosage curve in Fig. 1C shows that the polymer is also a secondary radiolytic product. Its total mass is low and at 170 Mrd accounts for about 3% of the mass of bicarbonate initially present. The HPLC measurements give only one large peak which increases with dose and corresponds to M_w 14000-16000 daltons. The infrared spectra consists mainly of broad bands which are common for polymeric material and difficult to assign; they show clearly that nitrogen is absent. Some other observations on acid hydrolysis and the dependence of temperature range on softening and melting suggest that it may be a composite material. More work is needed for its characterization.

4.5. Influence of pH and absorbed dose

At pH > 10 the concentrations of all radiolytic products decrease in a manner that is similar to the trend shown in the insert of Fig. 1B where the data for oxalate are given. It is worth noting also that the irradiations at large dose rates did not produce oxalic acid in carbonate solutions at pH > 10(1). This supports the present findings that the origin of formate and oxalate, and consequently of the secondary radiolytic products (formaldehyde and polymer) is in the reaction of the hydrated electron with carbon dioxide, which is present in the solution in equilibrium with the bicarbonate; at pH > 10 this equilibrium is shifted towards CO₃²⁻, and the absence of CO₂ explains the absence of organic compounds.

4.6. Ammonia

In a bicarbonate solution (5×10^{-2} mol dm⁻³, pH 7.8) about 25% of hydroxyl radicals disappear by reaction (11) producing NH₂ radicals. Our kinetic-spec-

trophotometric experiments suggest that the fate of the NH_2 radical is

and a rate constant of $(1.5 \pm 0.5) \times 10^9 \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$ is derived from the disappearance of CO_3^- , which was observed at 600 nm in experiments where the reactivity of hydroxyl radicals towards NH_3 and HCO_3^- were equal. Similar reactions of carbonate radical-ion by O-transfer were examined elsewhere⁽¹⁷⁾. The experiments also suggest the reaction

similar to that of CO_2^- (eq. 15), but with $k_{22} < 10^4 \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$. Other known reactions⁽¹⁸⁾ might also account for the disappearance of NH_2 , e.g.

or the reaction with hydrogen peroxide, $k(\text{NH}_2 + \text{H}_2\text{O}_2) = 9 \times 10^7 \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$. Nevertheless, the reaction (22) is the most likely fate of the NH_2 radical in γ -radiolysis, because of the very low concentrations of radicals in the irradiated solution. Hydroxylamine and hydrazine, if formed at all, decompose by forming ammonia and nitrogen as main radiolytic products, and nitrogen is not found in the organic radiolytic products or in the polymer.

4.7. Carbamate

Carbamate is present in ammonium carbonate solutions in equilibrium concentrations which depend on the total ammonium carbonate-carbamate concentration⁽¹⁴⁾. We have made pulsed electron beam experiments with 0.05 and 0.25 mol dm^{-3} solutions (pH 9.0 and 10.4) where the equilibrium concentrations of carbamate were estimated to be 7% and 50% respectively. In all samples, both argon or N_2O saturated; we found only the CO_3^- radical in amounts which are expected if only reactions (9)-(11) occur. We have concluded that under the working conditions either the carbamate takes no part in the reaction process or its reactions lead to the carbonate radical-ion, i.e. the same product as in the radiolysis of carbonate.

5. CONCLUDING REMARK

Radiation chemical reactivity of the bicarbonate ion is limited to its reaction with OH (eq. 9) which is followed by reactions leading efficiently to the re-formation of bicarbonate (eqs. 16-20). The synthesis of organic compounds in dilute aqueous solutions of bicarbonate (O_2 -free) is due to the reaction of the hydrated electron (eq. 8) with carbon dioxide which is present in the equilibrium with HCO_3^- , and the subsequent reactions of carboxyl radical-ions (eqs. 13-16).

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LEGEND

Figure 1.

Radiolytic products in aqueous solutions of 0.05 mol dm^{-3} bicarbonate, O_2 -free: **A.**- Formate, $G^\circ = 2.2$; **B.** - Oxalate, $G^\circ = 0.05$,
Insert: pH influence on the oxalate concentration measured at 13 Mrd;
C.- Polymeric material, M_w 14000-16000 daltons: the mass, g dm^{-3} (x); the peak area ($\times 10^6$) in HPLC analysis (●). The dotted lines show the initial trend computed by using CHEMSIMUL and the reactions (1)-(23).

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