

## Determination of the Rate Constants of the Reactions

### $\text{CO}_2 + \text{OH}^- \rightarrow \text{HCO}_3^-$ and Barbituric Acid $\rightarrow$ Barbiturate Anion $+ \text{H}^+$ Using the Pulse Radiolysis Technique

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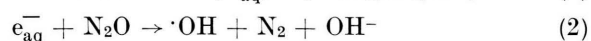
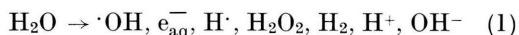
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Fast Reaction Kinetics, Pulse Conductometry, Peroxyl Radicals, Radiation Chemistry

The kinetics of the reactions of  $\text{CO}_2 + \text{OH}^- \rightarrow \text{HCO}_3^-$  (i) and barbituric acid  $\rightarrow$  barbiturate anion  $+ \text{H}^+$  (ii) have been remeasured using as a new approach the pulse radiolysis technique with optical and conductivity detection. The rate constants obtained in the present study,  $k_i$  (21 °C) =  $6900 \pm 700 \text{ M}^{-1}\text{s}^{-1}$  and  $k_{ii}$  (19 °C) =  $22 \pm 2 \text{ s}^{-1}$  agree within experimental errors with values obtained earlier by other methods.

## Introduction

In general radiation techniques are used to determine rate constants of free radical reactions. Ionizing radiation, *e.g.* high energy electrons from a Van de Graaff accelerator, produces in water  $\cdot\text{OH}$  radicals, solvated electrons ( $e_{\text{aq}}^-$ ) and H atoms as reactive species (reaction (1)). With  $\text{N}_2\text{O}$  the solvated electrons are converted into OH radicals (reaction (2)).



Under such conditions about 90% of the radicals are  $\cdot\text{OH}$  radicals and only 10% H atoms. Electron pulses can be delivered within a very short period. Thus the kinetics of the reactions of these free radicals can be followed either by spectroscopy or by conductometry, if charged species are involved. Because these measurements can be quite accurately done, OH radicals, solvated electrons and H atoms are species for which the most complete set of kinetic data are available. In most cases free radical reactions are very fast, often practically diffusion controlled. Thus products (which are no longer free radicals) are formed within a rather short time. These products are not always in equilibrium with their surroundings and, if subsequent reactions are comparatively slow, their reactions can be followed kinetically after the radicals have decayed.

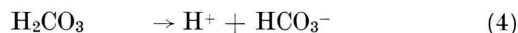
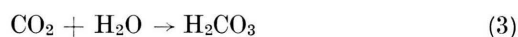
Here we report two examples of reactions whose kinetics have been well established by other tech-

niques, the reaction of carbon dioxide with the hydroxide ion [1] and the dissociation of barbituric acid [2, 3]. The pulse radiolysis technique allows to determine these values by another independent way.

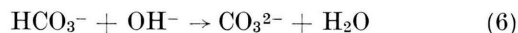
## Results and Discussion

*The reaction  $\text{CO}_2 + \text{OH}^- \rightarrow \text{HCO}_3^-$*

The hydration of  $\text{CO}_2$  has been extensively studied (for a review see Ref. [1]). At neutral pH reactions (3) and (4) predominate.



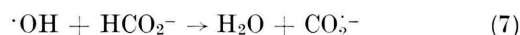
The hydration of carbon dioxide is quite slow ( $k_3 = 0.03 \text{ s}^{-1}$  at 25 °C). The subsequent dissociation of the carbonic acid (reaction (4)) is comparatively instantaneous [1]. At alkaline pH reactions (5) and (6) gain in importance.



The rate determining step is reaction (5) ( $k_5 = 6300 \text{ M}^{-1}\text{s}^{-1}$  at 21 °C), reaction (6) being several orders of magnitude faster [1].

With the help of the pulse radiolysis technique reaction (5) can be conveniently determined as follows.

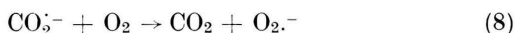
Using a 4:1 mixture of  $\text{N}_2\text{O}$  and  $\text{O}_2$  to saturate an aqueous solution of sodium formate ( $3 \times 10^{-4} \text{ M}$ ) and  $4 \mu\text{s}$   $e^-$ -pulses of  $\sim 30 \text{ Gy}$ , OH radicals are formed according to reactions (1) and (2). These OH radicals abstract an H atom from formate (reaction (7))



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The majority of the H atoms is scavenged by  $O_2$  to give  $HO_2$  (in basic solutions  $O_2^{\cdot-}$ ,  $pK_a = 4.75$ ) [4].

The resulting  $CO_2^{\cdot-}$  radical rapidly ( $k \approx 2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ ) transfers an electron to  $O_2$  (reaction (8)), possibly *via* a very short-lived ( $\tau_{1/2} \leq 4 \mu\text{s}$ ) and not yet detected peroxy radical ( $O_2^{\cdot-}CO_2^{\cdot-}$ ).



Thus  $CO_2$  has been created *in situ* within  $\sim 1\text{--}2 \mu\text{s}$  after the pulse. Reaction (7) and (8) are not connected with a measurable change in conductivity because  $HCO_2^{\cdot-}$ ,  $CO_2^{\cdot-}$  and  $O_2^{\cdot-}$  have about the same equivalent conductance.

However, if in alkaline solution  $CO_2$  reacts with  $OH^-$  to give  $HCO_3^-$  (reaction (5)) the highly conducting  $OH^-$  ( $\lambda^\circ = 179 \Omega^{-1} \text{ cm}^2$  at  $20^\circ \text{C}$ ) is substituted by the less conducting  $HCO_3^-$  ( $\lambda^\circ$  ( $20^\circ \text{C}$ ) =  $41 \Omega^{-1} \text{ cm}^2$ ).

Thus a drop in conductivity is observed as the reaction proceeds (Fig. 1). At  $\text{pH} \geq 10$  the reaction is kinetically of first order, by a 30 Gy pulse only  $\sim 1.7 \times 10^{-5} \text{ M}$  of  $CO_2$  are formed and  $OH^-$  concentration is always in excess. The inset in Fig. 1

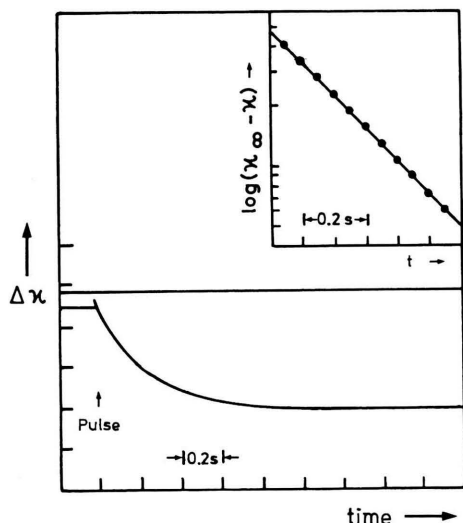


Fig. 1. Conductivity change as function of time following a  $4 \mu\text{s}$ -pulse in a  $N_2O/O_2$ -saturated  $0.3 \text{ mM}$  sodium formate solution at  $\text{pH } 10.7$ . Inset: the corresponding first-order kinetic plot.

shows the corresponding first order plot. The kinetics at other  $\text{pH}$  values have been obtained similarly and  $k_{\text{obs}}$  vs. the hydroxide ion concentration are plotted in Fig. 2. From the slope of the curve the second order rate constant  $k_5 = 6900$

$\text{M}^{-1}\text{s}^{-1}$  at  $21^\circ \text{C}$  is calculated (estimated error:  $\pm 10\%$ ). It agrees within experimental error with values that have been found by using different techniques (see review Ref. [1]).

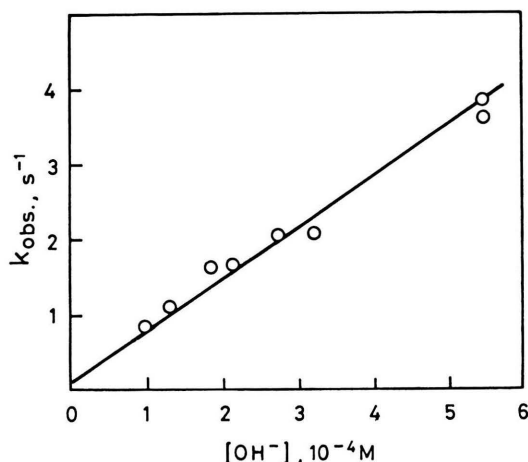
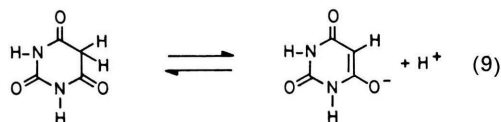


Fig. 2. The  $OH^-$ -concentration dependence of the observed first-order rate constants of conductivity changes in sodium formate solutions at  $21^\circ \text{C}$ .

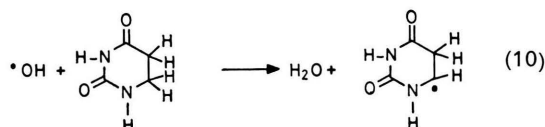
The reaction *barbituric acid*  $\rightarrow$  *barbiturate ion* +  $H^+$

Barbituric acid is not a very weak acid ( $pK_a = 4.0$ ), but being a C-H acid it dissociates only slowly (reaction (9)) (for details see Refs. [2] and [3]).

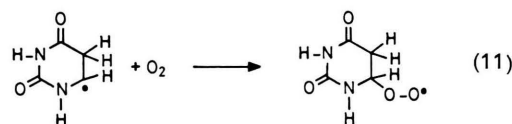


This acid can be generated by reacting dihydro-uracil with  $OH$  radicals (reactions (1) and (2)) in the presence of oxygen [5].

The predominant attack of the  $OH$  radical is at C-6 (reaction (10)) [6].

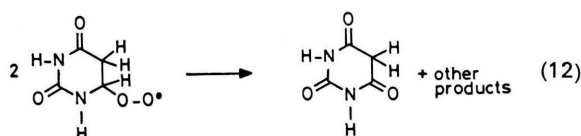


In the presence of oxygen the resulting radical is converted to the corresponding peroxy radical (reaction (11)).



Reactions (10) and (11) are very fast and occur practically within 5–10  $\mu$ s at the experimental conditions used. The bimolecular decay of the peroxy radical is comparatively slow ( $2k = 2 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ ), a reaction which can be followed by the decrease of absorption at 280 nm where these peroxy radicals weakly absorb. At an initial peroxy radical concentration of  $10^{-5} \text{ M}$  one can consider this reaction to be sufficiently complete after 10 ms.

A major product of this bimolecular decay (reaction (12)) is barbituric acid in its keto form.



Barbituric acid in its keto form only absorbs negligibly at 260 nm ( $\epsilon \leq 780 \text{ M}^{-1} \text{ cm}^{-1}$ ) [5] as do the other products (*e.g.* 5,6-dihydro-6-hydroxyuracil). However, on dissociation (eq. (9)) it forms a strongly absorbing species (barbiturate anion,  $\epsilon(260 \text{ nm}) = 20900 \text{ M}^{-1} \text{ cm}^{-1}$ ) [5] and a highly conducting proton.

After the bimolecular decay of the peroxy radicals (reaction (12)) one observes an increase in absorption at 260 nm with a half life of 31 ms. The

kinetics are of first order and a first order rate constant of  $k_9 = 22 \pm 2 \text{ s}^{-1}$  at 19 °C is calculated.

The build-up of a proton + anion as measured by the change of conductivity followed the same kinetics. These observations can be attributed to the dissociation of the keto form of barbituric acid (reaction (9)). The rate constant determined in the present study agrees within 10% with the value calculated from the data of the detailed study [3].

## Experimental

Sodium formate (Merck) and 5,6-dihydrouracil (Sigma) were recrystallized three times from triply-distilled water. Solutions of sodium formate ( $3 \times 10^{-4} \text{ M}$ ) and 5,6-dihydrouracil ( $10^{-3} \text{ M}$ ) in four time-distilled water were saturated with a gas mixture of  $\text{N}_2\text{O}/\text{O}_2$  (80:20 v/v) before irradiation. Pulses of 2.8 MeV electrons were generated by a Van de Graaff generator. The pulse durations were 2 or 4  $\mu$ s and the absorbed doses were between 15 and 30 Gy.

The optical detection system in our pulse radiolysis experiments has been described elsewhere [7]. For the detection of charged species a A.C.-conductivity method [8] was used in which two conductivity cells of identical geometry (one reference cell and one irradiation cell) are connected as two components of a Wheatstone bridge. The bridge is powered by a variable A.C. voltage of 10–40 V from a 10 MHz generator (both supplied by the Hahn-Meitner Institut für Kernforschung, Berlin).

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