

## Polarographic Determination of Diffusion Coefficients of Hydrogen Peroxide and Iron Chelates and Rate Constants of Hydroxyl Radical Reactions

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In previous notes <sup>1,2</sup> the rate constants of the reactions between hydrogen peroxide and different iron chelates have been calculated from polarographic experiments. These calculations cannot be carried out unless the diffusion coefficients of the different species and the stoichiometry of the reactions are known.

The stoichiometry is rather difficult to predict, as the hydroxyl radicals produced by the reaction between H<sub>2</sub>O<sub>2</sub> and iron(II)<sup>3</sup> are reacting with nearly every compound in the solution. Therefore it is common to use a scavenger in a concentration sufficient to pick up all the hydroxyl radicals. In order to find this concentration, it is necessary to know the rate constants of the reactions between the hydroxyl radicals and the different compounds in the solution.

This note presents the diffusion coefficients of H<sub>2</sub>O<sub>2</sub>, Fe<sup>3+</sup>, and some iron chelates, together with the rate constants of the reactions between hydroxyl radicals and acrylonitrile, EDTA (ethylenediamine-*N,N,N',N'*-tetraacetic acid), HEDTA (*N*-(2-hydroxyethyl)-ethylenediamine-*N,N'*,*N'*-triacetic acid), NTA (nitrilotriacetic acid), CyDTA (*trans*-1,2-cyclohexanediamine-*N,N,N',N'*-tetraacetic acid), acetic acid, and monochloroacetic acid determined by polarography.

The diffusion coefficients shown in Table 1 have been determined by use of the Ilkovic equation. The figures for H<sub>2</sub>O<sub>2</sub> and Fe<sup>3+</sup> agrees with the literature.<sup>4,5</sup>

The rate constants of the reactions between hydroxyl radicals and the different compounds were calculated from competition experiments using Koutecky's ap-

Table 1. The diffusion coefficients of hydrogen peroxide, Fe<sup>3+</sup>, and different iron(III) chelates. Ionic strength 0.20.

Temp. °C	$D_{\text{H}_2\text{O}_2} \times 10^5$ cm <sup>2</sup> sec <sup>-1</sup>	$D_{\text{Fe}^{3+}} \times 10^6$ cm <sup>2</sup> sec <sup>-1</sup>	$D_{\text{Fe(III)-chelate}} \times 10^6$ cm <sup>2</sup> sec <sup>-1</sup>		
			$D_{\text{Fe(III)-EDTA}}$	$D_{\text{Fe(III)-HEDTA}}$	$D_{\text{Fe(III)-NTA}}$
10.0	0.88 ± 0.04	2.76 ± 0.05	3.02 ± 0.04		
20.0	1.35 ± 0.04	4.30 ± 0.06	4.61 ± 0.03		
30.0	1.75 ± 0.05	5.72 ± 0.06	6.04 ± 0.05		
40.0	2.20 ± 0.04	7.05 ± 0.07	7.58 ± 0.06		

proximated equation.<sup>6</sup> This equation predicts a 29% reduction of the limiting current, when the stoichiometry of the reaction between iron(II) and H<sub>2</sub>O<sub>2</sub> is altered from 2 to 1. Therefore, by adding increasing amounts of the compound to a mixture of iron and H<sub>2</sub>O<sub>2</sub> ([H<sub>2</sub>O<sub>2</sub>] = 50 × [iron]) and detecting the limiting current, it is possible to find the concentration of the compound able to reduce the limiting current by 29%. These experiments give the relative rate constants which are converted to absolute rate constants by comparing with the rate constant of acrylamide.<sup>7</sup>

Table 2. The relative and absolute rate constants of the reactions between hydroxyl radicals and different compounds (scavengers). Temp. 20.0°C. 1.0 M HClO<sub>4</sub>.

Scavenger	Relative rate constant	Absolute rate constant (mol/l) <sup>-1</sup> sec <sup>-1</sup>
Acrylonitrile	1.8	3.4 × 10 <sup>9</sup>
EDTA	2.2	4.2 × 10 <sup>9</sup>
HEDTA	1.9	3.6 × 10 <sup>9</sup>
NTA	0.36	6.8 × 10 <sup>8</sup>
CyDTA	2.0	3.8 × 10 <sup>9</sup>
CH <sub>3</sub> COOH	0.010	1.9 × 10 <sup>7</sup>
ClCH <sub>2</sub> COOH	0.012	2.3 × 10 <sup>7</sup>

Table 2 contains both the relative and absolute rate constants. The rate constants of acrylonitrile, acetic acid, and monochloroacetic acid are in good agreement with the literature.<sup>7,8</sup>

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The polarographic method is a simple one for determining rate constants of radicals but the absence of qualitative information about the radicals is, however, a great disadvantage.

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## Microwave Spectrum of Chlorobutatriene

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The simplest molecule containing three cumulated double bonds — butatriene — has been carefully studied by electron diffraction,<sup>1</sup> IR and Raman spectroscopy.<sup>2</sup> As butatriene itself has no permanent dipole moment it produces no pure rotational spectra. Chlorobutatriene, however, has a dipole moment and it is the only four carbon cumulene studied so far with microwave spectroscopy. The substance has been discovered by Vestin *et al.*<sup>3</sup> It is extremely unstable and difficult to handle.

The spectrum has been recorded in the region 25 000–40 000 MHz. It is very

complex but most of its lines are grouped together in bands at intervals of approximately 3 000 MHz. Each band begins abruptly on the low frequency side and continues for 500–600 MHz with decreasing intensity. There is also a repeated structure within the band. A typical band-head is shown in Fig. 1.

In order to solve the spectrum, a theoretical structure was proposed with butatriene C–C and C–H bond lengths,<sup>1</sup> vinylchloride C–Cl bond length,<sup>4</sup> the C–C–Cl angle 122° and all C–C–H angles 120°. See Fig. 2.

This gives an expected value of the asymmetry parameter  $\kappa = -0.992$  and from this chlorobutatriene is expected to be an almost prolate symmetric rotor. Consequently the regions of dense absorption are logically assigned to  $\Delta J = +1, \Delta K_{-1} = 0$  transitions which are active through the  $\mu_a$  dipole moment. CNDO calculations on the assumed structure give a theoretical dipole moment  $\mu_a = -2.05$ ,  $\mu_b = 0.44$  and  $\mu_c = 0$  debye.

The line abundance of the bands and the repeated structure with decreasing intensity within the bands indicate a low lying successively excited vibrational mode.

In Fig. 1 the labeling indicates the main peaks of the rotational bands in the vibrational states  $v = 0$  to  $v = 5$ . From fitting the relative intensities of the lines with those expected from the Boltzmann distribution law the fundamental frequency of the vibration was found to be  $100 \pm 50 \text{ cm}^{-1}$ .<sup>5</sup> The great error is due to the uncertainty in the intensity measurements. These vibrational satellites are presumably states in which the skeletal bending mode is excited.

High resolution spectra of the bands give evidence for other vibrational satellites.

The lines from the ground state have been assigned. Outside each group, lines were found which could be identified as  $K_{-1} = 0, 1$  and 2 transitions on the basis of their characteristic second-order (but unresolved) Stark effects. Within the band the transitions  $K_{-1} > 3$  were detected by their relative intensities and quadrupole splittings, which increase with  $K_{-1}$ . It is necessary to include the centrifugal distortion terms  $D_J$  and  $D_{JK}$ . The  $D_{JK}$  term makes an important contribution and reverses the normal ordering of the  $K_{-1}$  values.

The rotational constants are given in Table 1 together with those calculated from the hypothetical structure above.