

## The Far Ultraviolet Absorption Spectra and Ionization Potentials of the Ethyl Halides

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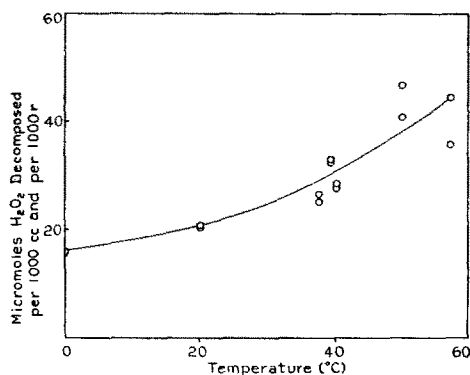


FIG. 2. Decomposition of hydrogen peroxide as a function of the temperature for an x-ray intensity of 3.0 r/sec. and a concentration of 1.0 millimole  $\text{H}_2\text{O}_2$  per 1000 cc.

tion (except when the concentration is very large)<sup>2, 8</sup> and with the inverse square root of the intensity, appears consistent with the experimental data. This would be in agreement with the present results if we assume that the decomposition in the case of x-rays is not due to the direct activation of the hydrogen peroxide molecules by the x-ray electrons, but that the primary process is the activation of water molecules<sup>1, 9-13</sup> followed by the transfer of energy from these activated molecules to the hydrogen peroxide.<sup>††</sup> On this assumption, the quantum efficiency (in the case of light) should be compared to the number of moles of hydrogen peroxide decomposed per unit of x-ray dosage. It should also be noted that if the decomposition were due to the direct activation of the hydrogen peroxide molecules by the x-ray electrons, in the extreme case as many as 10,000 molecules of hydrogen peroxide would be decomposed for each hydrogen peroxide molecule activated, an unlikely number in view of the relatively short chains observed in the case of light.

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\* I am indebted to Dr. E. R. Brownscombe for assisting with these measurements.

\*\* The decomposition of nonirradiated blanks was corrected for, and amounted, at 50°C, to a few percent of that produced during irradiation.

† For the decomposition by light, Allmand and Style, reference 2, found the temperature coefficient (at room temperature) to be: 1.42 for  $\lambda = 3650\text{\AA}$ , and 1.28 for  $\lambda = 2750\text{\AA}$ .

†† On this assumption, in our experiments the number of molecules of hydrogen peroxide activated would be expected<sup>1, 9-13</sup> to be of the order of  $10^{10}$ /cc/sec. With light, intensities producing from  $10^{10}$  to  $10^{16}$  activations/cc/sec. have been used.

<sup>1</sup> Fricke, J. Chem. Phys. 2, 556 (1934).

<sup>2</sup> Allmand and Style, J. Chem. Soc. (1930), 596, 606.

<sup>3</sup> Tian, Comptes rendus 151, 1040 (1910); 156, 1601, 1758, 1879 (1913).

<sup>4</sup> Henri and Wurmser, Comptes rendus 156, 1012 (1913); 157, 126 (1913).

<sup>5</sup> Kornfeld, Zeits. f. wiss. Phot. 21, 66 (1921).

<sup>6</sup> Wither, Trans. Faraday Soc. 21, 459 (1925).

<sup>7</sup> Heide, J. Am. Chem. Soc. 54, 2840 (1932).

<sup>8</sup> Qureshi and Rahman, Zeits. f. physik. Chemie 36, 664 (1932).

<sup>9</sup> Fricke and Morse, Phil. Mag. 7, 129 (1929).

<sup>10</sup> Fricke and Brownscombe, J. Am. Chem. Soc. 55, 2358 (1933).

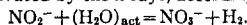
<sup>11</sup> Fricke and Brownscombe, Phys. Rev. 44, 240 (1933).

<sup>12</sup> Fricke and Hart, J. Chem. Phys. 2, 824 (1934).

<sup>13</sup> Fricke and Hart, J. Chem. Phys. 3, 60 (1935).

### The Oxidation of the Nitrite to the Nitrate Ion by the Irradiation of Its Aqueous Solutions with X-Rays

Gas-free solutions containing the nitrite ion were irradiated with x-rays and were analyzed for hydrogen and oxygen; and for nitrite by electrometric titration with potassium permanganate. The nitrite ion is oxidized to the nitrate ion and hydrogen liberated in the equivalent amount. The amount of nitrite oxidized is independent of the concentration of the nitrite ion from 0.05 to 100.0 millimoles/1000 cc and of the hydrogen ion concentration from pH = 2.0 to 11.0 and equals 0.55 micromole/1000 r/1000 cc. It is concluded that the transformation is due to water molecules activated by the x-rays, according to:



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### The Far Ultraviolet Absorption Spectra and Ionization Potentials of the Ethyl Halides

The absorption spectrum of ethyl iodide is essentially similar to that of methyl iodide<sup>1</sup> and starts at about the same wavelength. Two electronic series containing a large number of terms appear. The upper members can be extrapolated in the form of Rydberg series to ionization potentials of  $9.295 \pm 0.005$  and  $9.885 \pm 0.005$  volts. Thus a difference of about 0.6 volt is maintained in going from methyl to ethyl iodide though the ionization potentials of the latter are diminished by 0.2 volt relative to the corresponding ones in methyl iodide.

The first resonance bands of ethyl bromide start around 1770Å and thus suffer a short wavelength shift of 15Å relative to the corresponding bands in methyl bromide. They are much more diffuse but two series limits can still be observed. These can be extrapolated to the ionization potentials  $10.24 \pm 0.01$  and  $10.56 \pm 0.01$  volts corresponding to a diminution of 0.25 volt relative to the values obtained for methyl bromide.<sup>2</sup> Part of the difficulty of observing these limits is a background of continuous absorption arising from excitation in the CC bond.

In the case of ethyl chloride only the first few bands are sharp. These are shifted to long wavelengths by about 0.36 volt relative to the analogous bands in methyl chloride. The electronic difference of 0.08 volt is maintained and it is estimated that the ionization potentials of ethyl chloride are about 0.38 volt less than those given for methyl chloride.

The above data provide considerable support for the suggestion put forward by the author<sup>3</sup> that the dipoles of methyl and ethyl groups have a strong influence in reducing the ionization potentials of electrons in adjacent bonds. R. S. Mulliken<sup>4</sup> has shown that the spectra of the

alkyl halides are due to the excitation of nonbonding  $np\pi$  electrons from the halogen atom. It is here assumed that the additional strength of the  $C_2H_5$  dipole over the  $CH_3$  dipole is responsible for the diminution of the ionization potentials of the ethyl relative to the methyl halides. The increasing effect as we go from the iodide to the chloride is explained by the decreasing combination radii of the halogen atoms. This brings the dipole closer to the electron considered and thus increases its effect.

This dipole hypothesis has also been useful in explaining the deviations of the first few electronic states from Rydberg formulas which occur if the spectrum starts at fairly long wavelength (i.e., around 2000Å). These deviations are negligible in the case of  $C_2H_5$ ,  $H_2S$  and  $CH_3Cl$  which start around 1500–1600Å. In these cases the radii of the

orbits of the first excited states are so large that the effect of the dipole disappears after the first jump. In methyl and ethyl iodide the first and second excited states are still strongly affected by the dipole. The hypothesis can also be applied to give a satisfactory explanation of the magnitudes of the long wavelength shifts of the first resonance bands of the ethyl halides which appear to be a little anomalous at first sight.

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May 14, 1935.

<sup>1</sup> W. C. Price, Phys. Rev. **47**, 419 (1935).

<sup>2</sup> W. C. Price, Phys. Rev. **47**, 510 (1935).

<sup>3</sup> W. C. Price, J. Chem. Phys. **3**, 256 (1935).

<sup>4</sup> R. S. Mulliken, Phys. Rev. **47**, 413 (1935).