SUMMARY

An approximate theoretical picture, which leads to good agreement with experiment in some cases of physical adsorption on nonporous solids, is extended to adsorption in pores and on small spherical particles. The phenomena of capillary condensation and nucleation of condensation of a supersaturated gas are discussed in this connection.

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THE OXIDATION OF IODIDE TO IODINE BY DILUTE SOLUTIONS OF ORGANIC PEROXIDES

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Received November 17, 1949

Surprisingly little information is available concerning the kinetics of the oxidation of iodide to iodine by dilute aqueous solutions of specific organic peroxides. This situation exists in spite of the voluminous literature concerning the use of this reaction for the quantitative determination of various peroxides. During the course of the investigation of oxidizing substances in aqueous solutions condensed from the Los Angeles atmosphere, it became increasingly evident that a further knowledge of the kinetics of such reactions was indispensable for interpreting some of the data which had been obtained. Therefore, a study was made of the liberation of iodine from potassium iodide by dilute aqueous solutions of hydrogen peroxide, methyl hydroperoxide, ethyl hydroperoxide, *tert*-butyl hydroperoxide, and diethyl peroxide. The effects of changes in temperature, hydrogen-ion concentration, and iodide concentration were investigated.

MATERIALS

Methyl hydroperoxide and ethyl hydroperoxide, 3–4 per cent solutions in water, were prepared by C. Willard of the Stanford Research Institute according to the directions of Rieche and Hitz (5, 6). The mixture of diethyl peroxide and ethyl hydroperoxide, 35 per cent peroxide in ethyl ether, was prepared by C. M. Himel of the Stanford Research Institute according to the method of Rieche and Hitz (7). The *tert*-butyl hydroperoxide was a 70 per cent commercial sample from the Novadel-Agene Corporation, Buffalo, New York, which was distilled at atmospheric pressure through a Vigreux column. The hydrogen peroxide was prepared by diluting a 30 per cent Baker's C. P. analyzed product to 5 per cent and vacuum distilling the peroxide until 50 per cent of the solution was collected. The distillate contained about 0.036 per cent of hydrogen peroxide. The solutions were analyzed for hydroperoxides by adding 1 ml. to 1 ml. of concentrated sulfuric acid and 1 ml. of a saturated solution of potassium iodide in a small flask. After 2 hr. the liberated iodine was titrated with sodium thiosulfate. Blank determinations were also made and the values corrected for these blanks. The mixture of ethyl hydroperoxide and diethyl peroxide was also analyzed for total peroxide by heating with ferrous sulfate, concentrated sulfuric acid, and concentrated aqueous potassium iodide at 70°C. for 30 min. (10). The quantity of diethyl peroxide was assumed to be the difference between the peroxide contents found by the two methods. These analytical results were used in the preparation of the aqueous peroxide stock solutions which were of such concentration (about 0.0018 N) that the final equivalents of iodine liberated during the experimental runs did not vary more than 10 per cent among all the peroxides.[1] The potassium iodide, citric acid, and disodium hydrogen phosphate were all Baker's C. P. analyzed chemicals. All solutions were prepared with boiled conductivity water of specific conductivity less than 1×10^{-6} mhos/cm. at 25°C. This water had been redistilled through an all-glass still.

EXPERIMENTAL TECHNIQUE

Standard solutions of 0.1 M citric acid and 0.2 M disodium phosphate for McIlvaine's buffer were prepared as stock solutions. Sufficient quantities of each were added to the reaction apparatus (figure 1) to produce 100 ml. of the buffer at the desired pH. Twenty milliliters of the aqueous peroxide solution was added to the buffer in the apparatus. Suction was applied, the flask was evacuated, and oil-pumped nitrogen was allowed to bubble through the solution and fill the flask. After the fourth evacuation the flask was only partially filled with nitrogen. The apparatus was immersed in a thermostated water bath in a darkened room and sufficient time allowed for it to reach the bath temperature. A saturated aqueous solution of potassium iodide, usually 2 ml., was added, the flask was shaken, and the contents of the flask brought to atmospheric pressure by adding more nitrogen.

At appropriate time intervals 5 ml. of the reaction mixture was removed by

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[1] The very low concentrations of the peroxides were of the same order of magnitude as those of the oxidizing substances collected in the solutions condensed from the Los Angeles atmosphere. There are indications in the literature (8) that the kinetic study of the liberation of iodine from potassium iodide might yield, at low concentrations of peroxide, results that would be unexpected from the study at higher concentrations.

a calibrated pipet on the side of the apparatus and titrated with 0.01 *N* sodium thiosulfate from a microburet. Starch was used as indicator.

RESULTS

The results are shown in figure 2 and table 1. The rate of reaction of methyl hydroperoxide with potassium iodide to liberate iodine was determined for pH 4 and pH 7. The reaction, independent of pH between 4 and 7, was found to be of first order with respect to the peroxide. For ethyl hydroperoxide the variation in rate of reaction was examined for the effect of pH, amount of potassium iodide present, and temperature. Again a pH change between 4 and 7 did not alter the rate. However, the reaction rate was found to be directly proportional to the concentration of potassium iodide. Thus, the reaction of ethyl hydroperoxide (and probably of the other peroxides studied here) was actually of second order but appeared to be of first order because of the relatively large and therefore essentially constant concentration of potassium iodide.

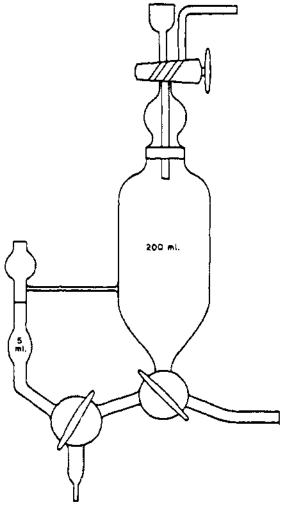

FIG. 1. The reaction cell

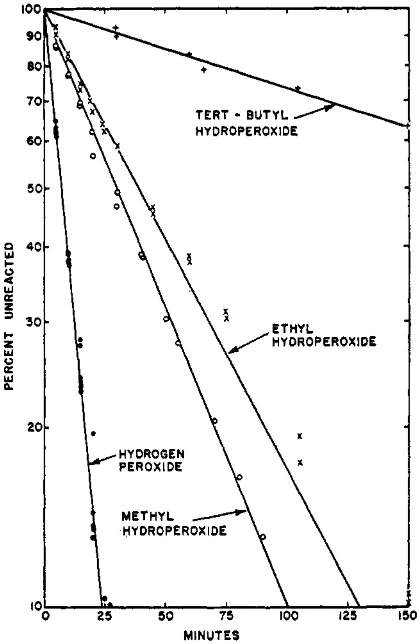

FIG. 2. Rates of reaction of four peroxides. Time plotted against per cent unreacted on log scale.

The effect of temperature on the reaction rate for ethyl hydroperoxide was determined. The heat of activation was estimated from the slope of the usual Arrhenius-type plot of the first-order reaction rate constant at constant potassium iodide concentration. The activation energy was found to be 12.7 kcal.

The titration values obtained were read to slightly better than one part in a hundred. An error of 1 or 2 per cent in either the final titration value and/or one intermediate value becomes magnified near the later state of reaction when the log of the amount unreacted is plotted against the time. Ethyl hydroperoxide deviates fairly widely from a straight line at over 50 per cent reacted at 30°C., with 2 ml. of saturated potassium iodide. However, the good linearity obtained with the other peroxides, as well as the linearity obtained with this peroxide at other potassium iodide concentrations and other temperatures, makes it appear likely that this is titration error (3 per cent error in total titration would remove the deviation).

TABLE 1

Rate constants calculated for the pseudo-first-order reactions

SUBSTANCE	INITIAL CONCENTRATION OF KI IN REACTION MIXTURE	INITIAL CONCENTRATION OF PEROXIDE*	pH	TEMPERATURE	*K*
	moles/liter	*milliequiv./liter*		°C.	*min.*$^{-1}$
Hydrogen peroxide	0.14	0.318	4	30	0.0909
Hydrogen peroxide†	0.14	0.318	4	30	0.0909
Hydrogen peroxide	0.14	0.280	7	30	0.0909
Hydrogen peroxide†	0.14	0.282	7	30	0.0909
Methyl hydroperoxide	0.14	0.307	4	30	0.0233
	0.14	0.307	7	30	0.0233
	0.28	0.308	4	30	0.0455
Ethyl hydroperoxide	0.07	0.272	7	30	0.0093
	0.14	0.296	7	30	0.0175
	0.14	0.298	4	30	0.0175
	0.28	0.298	7	30	0.0370
	0.14	0.221	4	20	0.0089
	0.14	0.267	7	35	0.0238
	0.14	0.275	7	40	0.0357
	0.14	0.267	7	50	0.0714
tert-Butyl hydroperoxide	0.14	0.313	4	30	0.003
	0.14	0.313	7	30	0.003

* Calculated from the number of equivalents of iodine liberated after reaction was relatively complete.

† Diluted from Baker's C.P. 3 per cent hydrogen peroxide and used without distilling.

For the purpose of comparison the reaction rate of hydrogen peroxide with potassium iodide was also investigated at these low concentrations. Again the reaction mixtures were buffered to pH 4 and pH 7. At the higher pH the final equivalents of iodine liberated were less than at pH 4, probably because of the catalytic decomposition of hydrogen peroxide by potassium iodide (2, 9). However, the same rate constant was obtained for both of the pH values. Also, the rate was independent of any preservatives that may have been present in the commercial hydrogen peroxide, as distillation of the peroxide failed to change the rate constant.

The reaction of *tert*-butyl hydroperoxide was studied at pH 4 and pH 7 and also found to be independent of the pH at the concentration used. Again it was found to be a pseudo-first-order reaction.

An attempt was made to determine the reaction rate of diethyl peroxide with potassium iodide. Rieche and Brumshagen (4) in 1928 noted that diethyl peroxide liberated iodine from potassium iodide only slowly and in 1949 Dickey *et al.* (1) found no reaction of di-*tert*-butyl peroxide with potassium iodide in acid solution.

The reaction of a mixture of ethyl hydroperoxide and diethyl peroxide with potassium iodide was studied at pH 4. The final equivalents of peroxide found corresponded only to the value of the ethyl hydroperoxide. The rate constant was also the same within experimental error as for pure ethyl hydroperoxide. Thus diethyl peroxide did not react at this pH in the time allowed.

The application of these results to the investigation of oxidizing substances in the air by the oxidation of organic materials. This oxidizing action of the solutions was found later to occur at a pH of 5 but only slightly, if at all, at a pH of 7. Therefore, the results of the present work show that the oxidizing substances could not have been organic peroxides, unless they differed radically from those discussed in this paper. There is reason to believe that part of this oxidizing action is caused by oxides of nitrogen.

SUMMARY

The reaction rate of ethyl hydroperoxide with potassium iodide to liberate iodine was studied at two pH values, three concentrations of potassium iodide, and five temperatures. Methyl hydroperoxide was studied at two pH values, and two potassium iodide concentrations. *tert*-Butyl hydroperoxide and hydrogen peroxide were investigated at pH 4 and pH 7. All reactions were found to be pseudo-first-order reactions independent of the pH (except for the decomposition effect noted with hydrogen peroxide). The activation energy of ethyl hydroperoxide was found to be 12.7 kcal.

The application of these results to the investigation of oxidizing substances in the Los Angeles atmosphere is discussed briefly.

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