rium are the same as those remote from equilibrium.

The authors are indebted to the W. K. Kellogg Radiation Laboratory at this Institute for the preparation of neutron sources used in this investigation.

Summary

Radioactive trivalent arsenic does not exchange with non-radioactive pentavalent arsenic in dilute acid or alkaline solutions in the absence of other easily oxidizable or reducible substances. In the presence of iodine in acid solution, however, an exchange takes place at a measurable rate. On the assumption that the exchange occurs through the oxidation and reduction of the iodine, we have calculated the rates of oxidation and reduction at chemical equilibrium from measurements of rates of exchange in systems containing iodide ion and small amounts of free iodine. The rates of oxidation and reduction measured in this way are in agreement with the kinetic expressions shown by Roebuck to hold for the same reactions remote from equilibrium, and lead to specific rate constants which agree with those measured by him.

PASADENA, CALIF. RECEIVED APRIL 7, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Effect of Iodine on the Rate of Decomposition of Ethylene Oxide

BY R. FRANCIS FAULL AND G. K. ROLLEFSON

In a previous investigation on the effect of iodine on the decomposition rate of acetaldehyde and propionaldehyde,[1] it was found that the decomposition mechanism could be divided into two parallel sets of reactions. The rate-determining step of the first set was a simple bimolecular reaction which depended only on the square of the initial iodine concentration. The second set consisted of a series of reactions such that the rate was first order with respect to the aldehyde concentration and one-half order with respect to the initial iodine concentration. This second series of reactions was essentially the catalysis of the decomposition of the aldehydes by free radicals and iodine atoms. Because the thermal decomposition of ethylene oxide was known to be free from reaction chains induced by free radicals,[2,3] the iodine catalyzed decomposition of ethylene oxide offered an interesting possibility to test the steady state theory advanced in the earlier paper.

At temperatures above 350° the addition of small amounts of iodine is found to cause a marked catalysis in the decomposition of gaseous ethylene oxide. Some typical results at 392.5° are shown in Fig. 1. The pressure increase is plotted as the ordinate against time as the abscissa. It is evident that during the major portion of the reaction the rate is independent of the concentration of the ethylene oxide. This steady state condition is in accord with the theory already advanced.

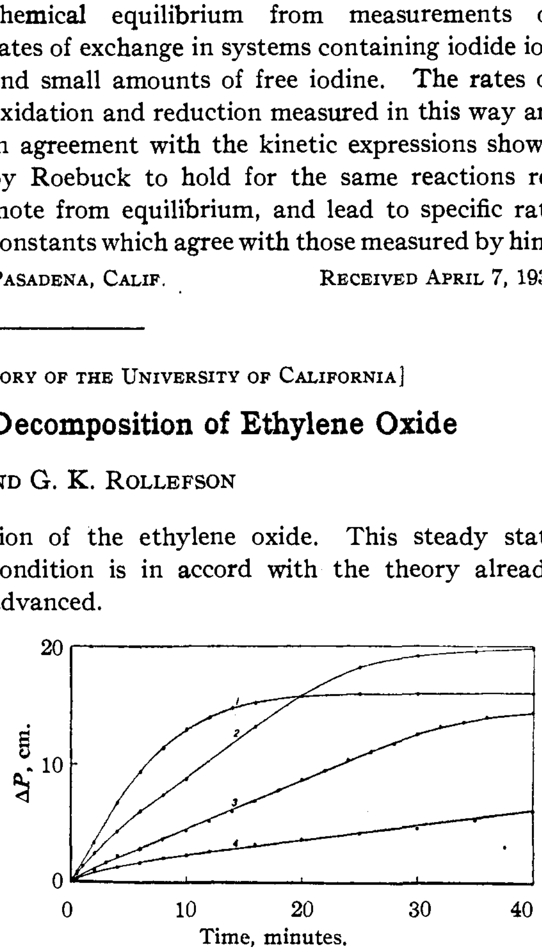

Fig. 1.—The curves show typical experiments at 392.5°. The initial concentiations are as follows:

Experiment	Ethylene oxide, cm.	Iodine, cm.
1	20.15	2.15
2	24.75	1.50
3	22.00	0.95
4	20.85	.65

The apparatus used and the experimental procedure were similar to that adopted in the aldehyde investigation. An analysis of the gaseous products was made using the methods of Leighton.[4-6] The results are summarized in Table I. The methane was identified by showing that combustion of the hydrocarbon gas left after the removal of carbon monoxide yielded two moles of water to one of carbon dioxide.

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(1) Rollefson and Faull, THIS JOURNAL, 59, 625 (1937).

(2) Rice and Rice, "The Aliphatic Free Radicals," The Johns Hopkins Press, Baltimore, 1935, p. 161.

(3) Fletcher and Rollefson, THIS JOURNAL, 58, 2135 (1936).

(4) Blacet and Leighton, *Ind. Eng. Chem., Anal. Ed.*, 3, 266 (1931).

(5) Blacet, MacDonald and Leighton, *ibid.*, 5, 272 (1933).

(6) Blacet and MacDonald, *ibid.*, 6, 334 (1934).

TABLE I

	CO_2	CO	H_2	CH_4	Higher hydro-carbons	Unsatu-rates
Unpacked vessel	<1%	47%	None	50%	None	<2%
Packed vessel	<2%	50%	None	Mixture with not more than one-half methane		<2%

(The gas smelled faintly of aldehyde.)

The pressure increase during a decomposition reaction never reaches the theoretical end-point of twice the initial pressure, but approaches to about 80% of the theoretical value. This discrepancy is attributed to a simultaneous polymerization reaction accompanying the decomposition, as any other type of reaction would upset the equivalence of methane and carbon monoxide shown by our analysis.

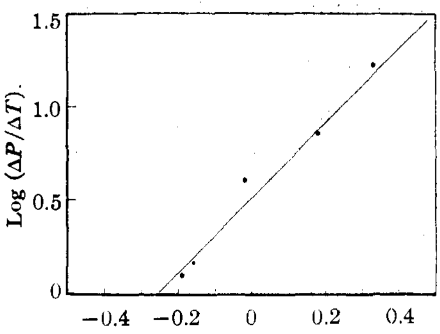

Fig. 2.—The line is drawn with a theoretical slope of two, and the validity of the square law is shown by the correspondence of the observed points to the line.

To test the reaction for homogeneity some experiments were performed in a reaction vessel packed with small diameter glass tubing. In this vessel the surface was increased more than ten times while the average distance to the wall was decreased more than ten times. Under these conditions the rate of pressure change was observed to be about ten times greater than in the unpacked vessel. The final pressure increase in these experiments was found to be only about 50 or 60% of the theoretical value, indicating that an increase of surface accelerated the polymerization more than the decomposition. It is evident from the analysis of the products that the reaction in the packed vessel included some reaction other than the simple decomposition found in the unpacked vessel. If the surface–volume ratio was changed by increasing the size of the reaction vessel the rate was not affected appreciably. This fact may be taken as evidence that in the unpacked vessel any surface effects are of minor significance. As a further test of the assumption that the main reaction in the unpacked vessel is homogeneous, nitrogen was introduced into the system during the course of a reaction. The introduction of slightly more than one-third of an atmosphere of nitrogen into a mixture of 20 cm. of ethylene oxide and 0.4 cm. of iodine had no effect on the rate of decomposition as measured by pressure change except for a very slight initial disturbance. If the reaction were heterogeneous it would be expected that the rate would be decreased because of the increased time required for the reactants to diffuse to the walls in the presence of the nitrogen. This absence of any effect of nitrogen accompanied by the excellent reproducibility of the rate constants in different vessels leads to the conclusion that the reaction in the unpacked vessel is mainly homogeneous.

The kinetics of the iodine catalyzed decomposition appear to be quite simple. Within a few minutes after the beginning of the reaction, the iodine color has disappeared from the reaction vessel and the system is in a steady state where the rate determining step is the one that regenerates iodine. This condition exists as long as the concentration of ethylene oxide is at least three times greater than the iodine added. As there is very little free iodine present in the steady state, we may assume that the concentrations of the reactants that are regenerating iodine are proportional to the initial iodine concentration. The slopes of the decomposition curves during the steady state are found to be proportional to the square of the concentration of the iodine added and independent of the ethylene oxide; see Fig. 2. The decomposition during the steady state, therefore, may be represented by

$$-\mathrm{d}((\mathrm{CH_2})_2\mathrm{O})/\mathrm{d}t = k(\mathrm{I_2})_0^2$$

The rate constants calculated according to this equation are listed in Table II. This rate law

TABLE II

Observed rate, cm./min.	$(I_2)_0$, cm.	k, 1/cm. × min.
0.125	0.65	0.296
.145	.69	.305
.730	1.50	.314
1.68	2.15	.363

would correspond to a mechanism in which the rate-determining step is a bimolecular reaction; the concentration of each of the reactants in this step is proportional to the initial concentration of the iodine. As the net reaction is the decomposition of ethylene oxide into carbon monoxide and methane, this mechanism may be represented formally by

$$(CH_2)_2O + I_2 = XI + YI \qquad (1)$$
$$XI + YI = CO + CH_4 + I_2 \qquad (2)$$

in which (2) is assumed to be the slow step.

All attempts to isolate the intermediate products failed because at lower temperatures the reaction rates are changed so that most of the iodine is in form of the free element. However, a few possibilities may be eliminated by comparing the observed decomposition rate with the rate of formation of iodine from several reactions. The reaction between methyl iodide and hydrogen iodide as calculated from Ogg's data[7] is definitely too fast to account for the observed results. Furthermore, it is mainly a first-order reaction at these temperatures because the second term in his rate law accounts for the major portion of the reaction. However, our observed results definitely require a second-order reaction. The reaction between methylene iodide and hydrogen iodide was also found to be too fast. It is reasonable to assume that hydrogen iodide is one of the intermediates involved in the decomposition mechanism. However, the results of a test of this made by adding a small amount of hydrogen iodide to the reaction mixture would be inconclusive due to the fact that hydrogen iodide alone causes some catalysis of the decomposition of ethylene oxide.

Summary

It has been shown that the decomposition of ethylene oxide into methane and carbon monoxide above 350° is catalyzed by iodine. Throughout the major portion of the reaction the rate is a constant which is determined by the square of the pressure of iodine originally added. Although it was not found possible to identify the intermediate stages it was shown that the results are in accordance with the theory of compensating reactions discussed in an earlier paper.

BERKELEY, CALIF. RECEIVED APRIL 27, 1937

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[7] Ogg, THIS JOURNAL, 56, 526 (1934).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE, AND THE PARKE, DAVIS & COMPANY RESEARCH LABORATORIES]

Sterols. XIV. Pyroandrosterone and Derivatives

BY RUSSELL E. MARKER, OLIVER KAMM, DAVID M. JONES AND LAWSON W. MIXON

The oxidation of beta-cholestanol by means of chromic acid gives a dicarboxylic acid[1] which when heated with acetic anhydride followed by pyrolysis is converted to pyrocholestanone, in which the first ring has lost one carbon atom and becomes a five-membered ring.

In order to determine the position of the double bond in neocholestene, which is formed by treating cholestyl chloride with quinoline, we oxidized this product both by chromic acid and by ozonolysis, obtaining the same dicarboxylic acid as when beta-cholestanol is oxidized. This shows that the double bond in neocholestene lies in the Δ-2 position.

The dicarboxylic acid from β-cholestanol was pyrolyzed to pyrocholestanone. Upon reduction of pyrocholestanone with sodium–alcohol, a mixture of pyro-beta-cholestanol and pyro-*epi*-cholestanol was obtained in the ratio of 3:1. The components were separated by means of digitonin, the compound of pyro-beta-cholestanol precipitating, whereas the *epi* form did not form a digitonide. Reduction of pyrocholestanone with aluminum isopropylate produced principally the *epi* form in the ratio of 2:1.

During the course of this work it was found that contrary to the generally accepted belief that only carbinols of the sterol series having the −OH group of the cholesterol configuration form insoluble complexes with digitonin, pyrocholestanone, a ketone, gave a heavy precipitate with digitonin in ethyl alcohol. This was also the case with β-cholestanone.

To produce pyroandrosterone derivatives for testing androgenic activity, the side chain of a mixture of the acetates of pyro-beta-cholestanol and pyro-*epi*-cholestanol (aluminum isopropylate) was oxidized with chromic acid. A mixture of

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[1] Windaus and Uibrig, *Ber.*, 47, 2387 (1914).