Adsorption runs 58 and 65 on preparation 3C were performed on zinc oxide surfaces which had been saturated with water vapor in the manner just described. The other runs were made on freshly evacuated surfaces. The gases employed in runs 52, 54, 58, 59, 62, 64 and 65 were free from water vapor. The hydrogen employed in run 55 contained 4.5 mm. of water vapor and that in run 56, 14.5 mm.

It is observed that rates of adsorption of both hydrogen and carbon monoxide are markedly smaller on surfaces saturated with water vapor. On the other hand, partial pressures of water vapor up to 14.5 mm. may be introduced with hydrogen without sensibly affecting the rate of adsorption. At 218° the dead space in the catalyst bulb of preparation 3C amounts to about 20 cc. In run 56, this 20 cc. of gas contains 0.4 cc. (N. T. P.) of water vapor. In the light of earlier considerations this entire quantity would be adsorbed immediately but only by those portions of zinc oxide very near the inlet tube. Since about 7.4 cc. of water vapor can be absorbed with great tenacity, from 5 to 10% of the surface is in the condition of the whole surface in run 58, whereas the remainder of the surface is unaffected. Such variation is within the experimental error set by the reproducibility of the surface.

Similar results were obtained on preparation 3B in regard to the effect of water vapor on the rate of adsorption of hydrogen. At 254° and 0.5 atm. pressure, preliminary saturation of the surface with water vapor reduced the rate of adsorption by 75%.

Because, in the presence of nickel, deuterium exchanges very much more rapidly with benzene than does deuterium oxide, Horiuti and Polanyi[7] consider that the exchange does not proceed by dissociative adsorption succeeded by recombination of the fragments, unless equilibrium conditions on the surface are upset by a change from deuterium to deuterium oxide.

On the basis of common examples of poisoning and on the basis of the researches presented in the paper, the authors consider that water vapor in quantity may reduce reaction rates by reducing the rate of the activated adsorption of the reactants if such adsorption be rate determining, or by making unavailable a certain fraction of the catalytically effective surface if some succeeding step be rate determining. Thus the authors believe that the consideration whereby Horiuti and Polanyi reject the mechanism of exchange via dissociative adsorption is not valid.

Summary

1. Water vapor has been shown to minimize surface reduction of zinc oxide catalysts at lower temperatures.

2. Water vapor has been shown to be strongly adsorbed from gas mixtures containing this vapor by those fractions of zinc oxide surfaces to which the mixture of gases first has access.

3. Saturation of zinc oxide surfaces with water vapor has been shown markedly to inhibit the activated adsorption of hydrogen and carbon monoxide.

(7) Horiuti and Polanyi, *Trans. Faraday Soc.*, **30**, 1164 (1934).

The Behavior of Iodine in Some Sensitized Decompositions of Gaseous Organic Compounds

BY R. FRANCIS FAULL AND G. K. ROLLEFSON

Introduction

It has been shown by Hinshelwood and others[1-3] that the decomposition rates of a number of organic substances are greatly increased by the addition of relatively small amounts of iodine. In discussing their results they have discarded

(1) Bairstow and Hinshelwood, *Proc. Roy. Soc.* (London), **A142**, 77 (1933).

(2) Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," Oxford Univ. Press, London, 1933. p. 225.

(3) Bairstow, *Trans. Faraday Soc.*, **29**, 1227 (1933).

chemical mechanisms for the action of iodine in favor of a hypothesis involving collisions between iodine and the organic molecules. Recently, while preparing to test these reactions for photosensitivity, we have discovered that under the same conditions as prevailed in Hinshelwood's work little or no free iodine can be detected by spectroscopic methods during the course of the reactions. This result leads to the conclusion that these reactions actually proceed by chemical mechan-

isms and in this paper we wish to present evidence for three types of behavior.

Apparatus and Experimental Details

The apparatus consisted of a Pyrex reaction vessel of approximately 350-cc. capacity within an electric furnace. The reaction vessel was connected to an external vacuum system and to an iodine storage bulb, each through a heated glass valve.[4]

3 minutes
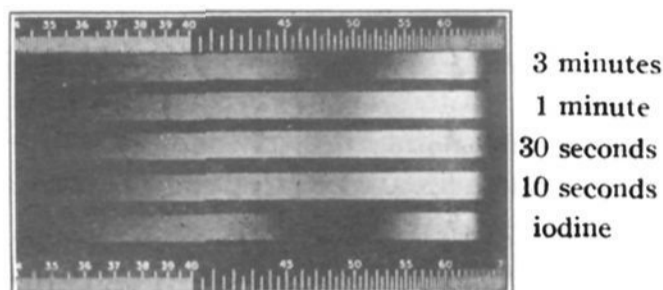1 minute
30 seconds
10 seconds
iodine

Plate I.—Propionaldehyde at 394°.

The glass valves eliminated troubles caused by ordinary grease stopcocks and were found to operate very satisfactorily in individual ovens, whereby the temperature could be maintained as high as 150°. The iodine storage bulb was immersed in a small oil-bath that could be heated to distil iodine into the reaction vessel. The pressure was measured by a click gage[5] and a mercury manometer. All connecting tubing was capillary glass, wound with resistance wire and electrically heated. The temperature was measured by a chromel–alumel thermocouple which was imbedded in a well extending into the center of the reaction vessel and could be regulated within one degree. The light source was a 500-watt tungsten projection lamp. By utilizing windows in the ends of the furnace the beam could be directed along a 15-cm. path through the reaction vessel into a Hilger E3 spectrograph.

The organic materials used were taken from the center fractions of redistillations of Eastman Kodak Co. stock and stored in three-liter bulbs connected to the vacuum line. The iodine was Merck reagent. In each experiment the iodine, at 1.5 cm. pressure, was introduced from the heated reservoir, the pressure measured and then the organic gas in question, at approximately 25 cm. pressure, was allowed to enter the reaction vessel.

Observations and Spectrograms

Acetaldehyde.—At 400° acetaldehyde removes the iodine color immediately upon entering the reaction vessel. The restoration of the color begins in about three minutes and is complete after five minutes. At 350° the reaction is slower, but at 300° the iodine color never completely disappears. All attempts to isolate an intermediate state failed because the iodine was liberated rapidly on cooling the reaction mixture. The reaction at 300° is photosensitive, the rate measured by pressure change being approximately doubled upon intense illumination with a 500-watt tungsten lamp.

(4) The glass valves were of a design supplied to one of us (G. K. R.) by Professor G. B. Kistiakowsky. They are similar to those which have been described by Bodenstein except that they have silver chloride on the valve seat which eliminates the necessity for grinding the movable parts very exactly.

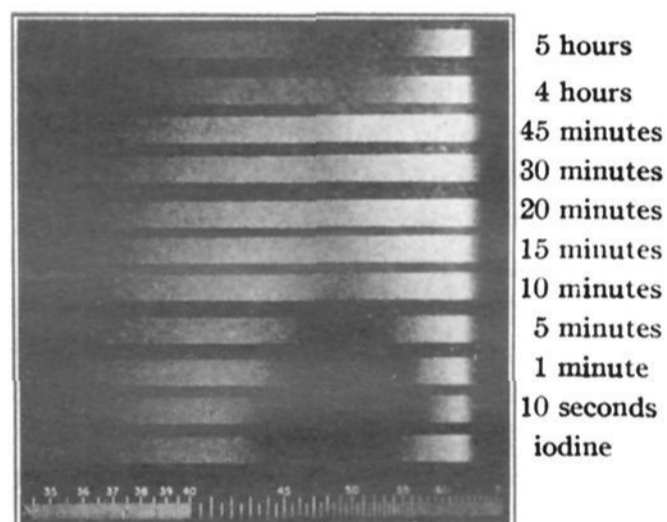(5) Smith and Taylor, THIS JOURNAL, **46**, 1393 (1924).

Propionaldehyde.—The same characteristics that are shown by acetaldehyde are exhibited by propionaldehyde (see Plate I). At 394° the color of the iodine disappears and returns within four minutes. At 340° the rate of reaction was increased by strong illumination as measured by pressure change.

Diethyl Ether.—At 440° the color of iodine disappears almost immediately and is completely restored after thirty or forty minutes.

Ethylene Oxide.—The behavior of ethylene oxide resembled closely that of acetaldehyde.

Methyl Alcohol.—At 470° methyl alcohol decolorized iodine within one minute. The color does not begin to return until after four hours have elapsed. The colorless reaction mixture can be removed without the liberation of iodine and can be shown to contain hydrogen iodide.

Methyl Formate.—At 460° methyl formate requires about fifteen minutes to decolorize the iodine (see Plate II). The color begins to return after three hours and is almost completely restored within five hours.

5 hours
4 hours
45 minutes
30 minutes
20 minutes
15 minutes
10 minutes
5 minutes
1 minute
10 seconds
iodine

Methyl Formate at 460°.

Plate II.—Spectrograms of different stages of iodine sensitized decompositions. The exposures are ten seconds, with a 500-watt lamp as a light source. Elapsed times are given from the beginning of the reactions. Scale units are in hundreds of Ångströms.

Formaldehyde.—At 450° the color disappears immediately and begins to reappear in about two hours. It is completely restored after five hours.

Diethylamine.—Diethylamine shows no decolorization of iodine over a wide temperature range within which it decomposes.

Discussion

The substances investigated fall into three distinct classes. The first consists of acetaldehyde, propionaldehyde, diethyl ether and ethylene oxide. The characteristics shown by these may be listed as follows: (1) the color of iodine disappears and returns within a short time; (2) no hydrogen iodide can be isolated during the course of the reaction; (3) the iodine absorption band disappears completely on the spectrograms
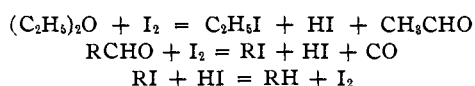
in some experiments; and (4) the decomposition products are the same in both the sensitized and unsensitized reactions.

The second class includes methyl alcohol, methyl formate and formaldehyde. The principal characteristics exhibited by these are as follows: (1) the color disappears rapidly but does not return for a relatively long period of time although the temperature is much higher than in Class I; (2) hydrogen iodide is present and can be isolated during the reaction; (3) the iodine absorption band is never completely removed from the spectrograms; and (4) the products in the iodine sensitized decompositions, except formaldehyde, are different from those in the unsensitized reactions.
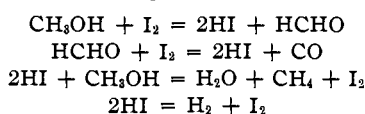
The third class, which includes diethylamine, shows no decolorization of the iodine, which may be due to the conditions being such that a high concentration of iodine exists at the steady state.

In both cases where the color of iodine disappears, the reaction is much too fast to be accounted for by a decomposition of the organic substance into hydrogen and a subsequent reaction between iodine and hydrogen.[6] The disappearance of the iodine therefore must be due to the formation of hydrogen iodide or an alkyl iodide.[7] On this basis the following equations for the first two classes may be proposed

<div align="center">

CLASS I

</div>

$$(C_2H_5)_2O + I_2 = C_2H_5I + HI + CH_3CHO$$
$$RCHO + I_2 = RI + HI + CO$$
$$RI + HI = RH + I_2$$

<div align="center">

CLASS II

</div>

$$CH_3OH + I_2 = 2HI + HCHO$$
$$HCHO + I_2 = 2HI + CO$$
$$2HI + CH_3OH = H_2O + CH_4 + I_2$$
$$2HI = H_2 + I_2$$

These equations account for the difference in the rate of reappearance of the iodine, because the reaction between an alkyl iodide and hydrogen iodide is rapid, whereas the decomposition of hydrogen iodide is slow.[6] A test of this is given by the rapid appearance of iodine color where

(6) Bodenstein, Z. physik. Chem., **29**, 295 (1899).

(7) The possibility of an addition compound between the organic substances and iodine may be ruled out by the following consideration. The entropy change in an addition reaction is always negative and from the change in the residual iodine concentration with temperature we must consider that ΔH for the formation of an addition product as an intermediate is positive. Therefore if we calculate $\Delta F_T^\circ = \Delta H - T \Delta S$ we find that the free energy change is positive and the equilibrium constant is less than one, which means that such an equilibrium could not account for the disappearance of the iodine.

methyl iodide is introduced into a reaction mixture containing hydrogen iodide at 365°. Methyl iodide itself does not begin to decompose appreciably until the temperature is well above 400°. A test reaction between hydrogen and iodine was found to be very slow at 450°, showing the absence of any catalytic effect in the apparatus. Therefore the essential difference between the two classes lies in the steps that produce iodine. Also the actual products present in the decomposition are accounted for by the equation.[8]

In any case it seems apparent that the sensitized decomposition takes place through definite chemical reactions rather than a collision activation process that was proposed by Hinshelwood.[1-3] In regard to Class I, it is known that acetaldehyde exists as an intermediate in the thermal decomposition of diethyl ether[9] and ethylene oxide,[10,11] and hence it is not unlikely that the sensitized decompositions go through an aldehyde stage. Even in Class II the formaldehyde intermediate has been reported in some of the thermal decompositions. In comparing the behavior of the two classes it appears that in Class II the course of reaction may go through a formaldehyde step rather than through any other aldehyde, the resulting slowness of the return of iodine color being due to the lack of formation of alkyl iodide from formaldehyde, as would have been the case if the decomposition had gone through any other aldehyde.

Our attention has been called to the work of Ogg [THIS JOURNAL, **56**, 526 (1934)] which makes it possible to calculate the rate of such a reaction as that between methyl iodide and hydrogen iodide under conditions such as prevail in the experiments referred to in this paper. According to the mechanism we have presented after the iodine color has disappeared the rate of decomposition of acetaldehyde is determined by the rate of the reaction between methyl iodide and hydrogen iodide. Using Ogg's equation for the rate as a function of temperature we calculate for one particular experiment at 420° [Hinshelwood, Proc. Roy. Soc. (London) A128, 89 (1930)] a rate of 1.83×10^{-8} mol./cc./sec. whereas the observed rate was 3.47×10^{-8} mol./cc./sec. when the reaction was approximately forty per cent.

(8) Bairstow and Hinshelwood, J. Chem. Soc., 1147 (1933).

(9) Newitt and Vernon, Proc. Roy. Soc. (London), **A135**, 307 (1932).

(10) Heckert and Mack, THIS JOURNAL, **51**, 2706 (1929).

(11) Fletcher, ibid., **58**, 539 (1936).

complete. This is as close agreement as could be expected.

Summary

The iodine concentration during a sensitized decomposition of gaseous diethyl ether, acetaldehyde, propionaldehyde, ethylene oxide, methyl alcohol, methyl formate, formaldehyde and probably many others, is very low.

The decompositions proceed through definite chemical reactions rather than collision activation processes.

Berkeley, Calif.   Received July 9, 1936

The Heat Capacity and Entropy of Barium Chloride Dihydrate from 15 to 300°K. The Heat of Solution of Barium Chloride Dihydrate. The Entropy of Barium Ion

By Oliver L. I. Brown, Wendell V. Smith and Wendell M. Latimer

The method of calculating the entropy of barium ion which has been used up to the present[1] involves directly the entropies of chloride, thallous and nitrate ions, and indirectly the entropies of silver, bromide and iodide ions. Since the entropy of chloride ion is known with greater precision than that of thallous and nitrate ions, a method of calculating barium ion directly from chloride ion has long been considered desirable. The recent careful work of Tippetts and Newton[2] on the thermodynamics of aqueous barium chloride solutions has now made such a calculation feasible. In the present paper we have determined the following properties of barium chloride dihydrate: (1) the entropy, (2) the heat of solution in water, and (3) the solubility in water. Combining these data we have calculated the entropy of barium ion in aqueous solution.

Material.—A c. p. grade of barium chloride was crystallized three times from redistilled water. It was then dried in a desiccator over partially dehydrated barium chloride dihydrate. Since the sample was found by analysis to have more than the theoretical amount of water, it was dried at 105°, then rehydrated in a desiccator containing water. After analysis showed that the sample had taken up more than the theoretical amount of water, the sample was again dried over partially dehydrated barium chloride dihydrate. This cycle was repeated once again before a sample containing the theoretical amount of water was obtained.

Heat Capacity Measurements.—The experimental method was that of Latimer and Greensfelder.[3] The apparatus was slightly modified from that used in previous work. The block employed to ensure a uniform temperature environment for the calorimeter was replaced by a new block, which was machined very carefully so as to provide better contact between the two halves of the block. The inner surface of the block was gold plated and polished, and reduced considerably the corrections necessary for heat interchange due to radiation. The approximate values of ΔT used in the measurements were: 1.2° up to 20°K., 2–3° up to 50°K., 3–6° up to 180°K, and 6–9° up to 300°K. In calculating the heat capacities one calorie was taken equal to 4.1833 int. joules, and the molecular weight of barium chloride diphydrate was taken as 244.317. Measurements were made on a sample of 192.845 g. (weight *in vacuo*). The results are given in Table I and shown as a function of temperature in Fig. 1.

TABLE I

MOLAL HEAT CAPACITY OF BARIUM CHLORIDE DIHYDRATE

$T.,$ °K.	C_p Cal./mole/deg.	$T.,$ °K.	C_p Cal./mole/deg.
14.87	1.06	112.10	22.87
16.18	1.27	117.92	23.53
17.24	1.49	123.62	24.16
20.00	2.04	129.49	24.94
23.16	2.73	135.64	25.81
25.69	3.36	141.68	26.46
28.14	3.97	147.84	27.09
30.21	4.51	153.76	27.65
32.13	5.05	160.01	28.21
34.87	5.89	166.86	28.77
37.98	6.82	173.45	29.34
40.45	7.39	180.25	29.95
42.91	8.26	187.15	30.63
48.02	9.63	193.41	31.06
51.15	10.57	200.27	31.63
54.60	11.54	207.32	32.11
58.06	12.51	214.06	32.57
61.78	13.38	221.02	32.97
66.12	14.45	229.72	33.45
69.82	15.35	236.41	33.78
70.78	15.58	244.76	34.58
73.92	16.31	254.54	35.02
78.67	17.33	263.58	35.33
83.68	18.31	272.18	36.01
89.08	19.30	281.17	36.48
94.72	20.26	287.97	36.65
100.61	21.21	297.07	37.09
106.37	22.00	301.28	37.13

(1) Latimer, Schutz and Hicks, *J. Chem. Phys.*, **2**, 82 (1933).

(2) Tippetts and Newton, This Journal, **56**, 1675 (1934); Newton and Tippetts, *ibid.*, **58**, 280 (1936).

(3) Latimer and Greensfelder, *ibid.*, **50**, 2202 (1928).