Summary

The four butenes, propylene and ethylene, all exceptionally pure, were quantitatively photoiodinated in chloroform at −55° in light of λλ 436, 546 and in two cases 644 mμ. Competing thermal reactions were paralyzed.

The quantum yields for the different olefins at −55° (concentrations and light intensity being the same) vary as much as fortyfold, due perhaps to a difference in the activation energy of a secondary thermal reaction common to all the photoiodinations.

Quantum yields at −55° fall off with decreasing frequency to a value of the order of 0.01 at λ 644 mμ.

The thermal reaction scheme of Schumacher does not harmonize with the photochemical results at −55°. The rate of photoiodination is more nearly in proportion to concentration of olefin and of iodine and to light intensity.

At low temperatures diiodobutane (presumably the 1,2-isomer) was prepared as a white solid in a state of reasonable purity, and photolyzed at −60, −20 and +25°. The quantum yield at 25° is nearly the same as that for symmetrical ethylene iodide.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Adsorption and Decomposition of Carbon Monoxide on Zinc Oxide Catalysts

BY ROBERT L. BURWELL, JR., AND HUGH S. TAYLOR

The results of an investigation into the rate of the activated adsorption of hydrogen at constant pressure on zinc oxide have been reported by Taylor and Strother.[1] It appeared desirable to extend this work by studying the rate of the activated adsorption of carbon monoxide on the same catalyst.

Experimental

Accordingly the technique and the apparatus of Taylor and Strother were employed. Zinc oxide was prepared in the manner described in their communication. Carbon monoxide was prepared by dropping formic acid into hot sulfuric acid. The effluent gas was passed successively over copper wool heated to 450°, soda lime, calcium chloride and phosphorus pentoxide.

The observed rates of adsorption fell off progressively with an accompanying change in color of the adsorbents from pure white to gray. The results of typical rate determinations are listed in Table I.

TABLE I

RATES OF ADSORPTION OF CARBON MONOXIDE ON 22.7 G. OF ZINC OXIDE, PREPARATION 3C, AT A PRESSURE OF ONE ATMOSPHERE

	Adsorption in cc., N. T. P.							
Time, min.	2	4	8	12	20	40	60	100
Run 6 184°	2.1	2,75	3.45	4.0	4.7	5.9	6.75	7.9
Run 7 218°	3.45	4.45	5.7	6.55	7.85	9.8	11.1	12.9
Run 8 184°	1.9	2.45	3.2	3.65	4.35	5.4	6.1	7.15

Twenty-one runs in all were made on preparation 3C at the two temperatures listed in Table I. They were similar to the ones in the table and showed a progressive deactivation of the catalyst surface. Similar results were obtained on another zinc oxide sample, preparation 3B. Hydrogen was then substituted for carbon monoxide and a number of rates of adsorption of that gas were determined at temperatures of 184 and 218°. After a few runs it was observed that the initial white color of the adsorbent had been regenerated. Adsorptions of hydrogen were very much greater and more rapid during the first few runs than in the subsequent ones.

These phenomena may be explained plausibly by the assumption that carbon monoxide is decomposed on the catalyst surface in accordance with the equation

$$2CO \longrightarrow C + CO_2$$

On admission of hydrogen, the deposited carbon is assumed to react to produce methane. Such a mechanism may account for the small amount of methane produced by similar catalysts in the methanol synthesis.[2] The decomposition of carbon monoxide corresponds to a considerable decrease in the free energy of the system at the temperatures under consideration.[3] Such a decomposition of carbon monoxide has been reported for other oxide catalysts.[4]

To test this hypothesis, an apparatus was constructed which permitted the passage of carbon monoxide over copper wool at a temperature of 400°, then successively through two spiral bubbling bottles containing solutions of barium hydroxide (no turbidity ever appeared in the second bottle), a tube containing calcium chloride and one containing phosphorus pentoxide. The gas passed thence through a tube containing 15 g. of zinc oxide. The off gas was passed through a bubbling tube into which a solution of barium hydroxide could be directly filtered and thence through a bubbling bottle containing barium hydroxide.

(1) Tank nitrogen purified in a manner similar to that of carbon monoxide, was passed over the sample of zinc

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[1] Taylor and Strother, THIS JOURNAL, 56, 586 (1934).

[2] Rideal–Taylor, "Catalysis in Theory and Practice," The Macmillan Co., London, 1926, p. 257 *et seq.*

[3] Lewis and Randall, "Thermodynamics," 1923, p. 573.

[4] H. Göthel in "Grenzflächen-katalyse," by M. Kroger, S. Hirzel, Leipzig, 1933, p. 104.

oxide maintained at a temperature of 425–450° for twenty hours at a rate of 2 to 5 cc. per minute. The catalyst was cooled to room temperature and the apparatus was flushed out with carbon monoxide. The temperature of the catalyst was elevated and maintained at 184° by means of an aniline vapor-bath. Barium hydroxide solution was inserted in the test bubbler. Turbidity appeared in ninety minutes.

The catalyst was cooled to 20° and the system was flushed out with nitrogen. The temperature was elevated gradually by means of a furnace. Turbidity appeared in a fresh barium hydroxide solution at 175°. Larger amounts of barium carbonate appeared as the temperature rose. The bulk of the precipitate formed between 340 and 400°.

The nitrogen passage was continued at a rate of 4 cc. per minute. After fourteen hours with the temperature of the catalyst maintained at 435°, no turbidity appeared in fresh barium hydroxide solution in two hours.

(2) The catalyst was cooled to room temperature and carbon monoxide passed through the system for twenty hours. No turbidity was evident in the test bubbler. On elevating the temperature to 184° faint turbidity appeared only after twelve hours.

Nitrogen was substituted for carbon monoxide and the temperature of the catalyst elevated in the same fashion as described in (1). Similar results were obtained. After nitrogen passage for four hours over the catalyst maintained at 420°, new barium hydroxide was inserted in the test bubbler. The temperature of the catalyst and the rate of nitrogen passage were continued. No turbidity was evident after twelve hours.

(3) The sequence of operations described in (2) was repeated. Results were similar save that forty-eight hours were required for the appearance of a faint turbidity at 184°.

(4) Carbon monoxide was passed through the system to displace the nitrogen with the temperature of the catalyst held at 300°. With fresh barium hydroxide solution in the test bubbler, turbidity appeared in half an hour. With the temperature of the catalyst at 370°, fresh barium hydroxide solution gave an immediate precipitate.

(5) During these experiments the catalyst had become markedly gray-brown. Hydrogen was passed over the catalyst for ten hours at 385°. The color of the catalyst lightened considerably and appeared a light gray.

Discussion

The experiments described in (1) to (5) demonstrate that carbon monoxide is in some degree decomposed to carbon dioxide in passage over active zinc oxide catalysts at temperatures above 184°. Only a small part of this carbon dioxide could be ascribed to an oxidation of carbon monoxide by zinc oxide.[5] In the course of the work described in (1) to (5) and especially in (4) large volumes of carbon dioxide were formed. Had such a volume of carbon dioxide been produced by the reduction of zinc oxide, a corresponding amount of zinc should have sublimed into the off tube. No such quantity was observed. It is further impossible to account by such an assumption for the effect of hydrogen in restoring the color of the catalyst.

The fall in catalytic activity of the zinc oxide surface as exemplified by the increasing times required to produce turbidity at a temperature of 184° may be presumed partially at least to have resulted from a covering of the "active spots" by carbon.

The slow reaction in the adsorption process cannot, however, have been the decomposition of carbon monoxide with subsequent adsorption of the carbon dioxide so produced. For were this true, zinc oxide could not act as a catalyst in the methanol synthesis. Further, were all of the adsorbed carbon monoxide to have been decomposed, one would expect all of the active surface to have been covered with carbon in the course of several runs, whereas the adsorption was still 40% of its initial value after twenty-one runs. From the excess hydrogen adsorbed in the first couple of runs after its substitution for carbon monoxide one may estimate that no more than about 15% of the carbon monoxide adsorbed during the twenty-one runs could have been decomposed.

Though it is clear that the observed rates of adsorption refer essentially to the activated adsorption of carbon monoxide on zinc oxide, the disturbing influence of the decomposition reaction renders unreliable any calculation of activation energies for the process. However, the activation energies appear somewhat higher than those reported by Taylor and Strother[1] for the adsorption of hydrogen on the same catalyst.

Garner and Maggs[6] have reported recently their inability to detect any activated adsorption of carbon monoxide on zinc oxide at temperatures up to 313° A. They conclude: "The absence of a discontinuity" (in the adsorption isobar) "in the case of carbon monoxide on zinc oxide supports the contention that such discontinuities do not occur in the absence of capillary flow." It is difficult to understand how the mere presence or absence of activated adsorption can decide which of the various theories of the mechanism of activated adsorption is correct. In any case had Garner proceeded to measurements at higher temperatures, he would have discovered the presence of activated adsorption.

In 1931, Taylor[7] pointed out that certain steps

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[5] Burwell and Taylor, THIS JOURNAL, **58**, 1753 (1936).

[6] Garner and Maggs, *Trans. Faraday Soc.*, **32**, 1774 (1936).

[7] Taylor, THIS JOURNAL, **53**, 578 (1931).

in many sorption processes must involve activation energies frequently of a considerable magnitude. It was at first thought that the rate determining step was the approach of the gas molecule to the surface. That such could not universally be true was indicated by the work of Pace and Taylor[8] and by that of Kohlschuetter[9] demonstrating that, at a pressure of one atmosphere and within limited temperature ranges, hydrogen and deuterium were adsorbed with the same velocity on zinc chromite, nickel, and chromium oxide gel, and by the work of Burwell and Taylor[10] on the effect of pressure on the rate of the activated adsorption of hydrogen on chromium oxide gel.

Garner[6,11] has recently reiterated the contention that in general the slow process in activated adsorption is the "diffusion" of the gas down capillaries from an initial rapid adsorption, a view that derives initially from Ward.[12] The application of the term "diffusion" to the suggested mechanism is misleading since whereas true diffusion increases with the temperature as $\sqrt{T}$, the hypothesized "diffusion" of Ward and Garner increases very much more rapidly. Lennard-Jones[13] has shown that to account for the large temperature coefficient it is necessary to assume that before diffusion can take place, a molecule must be raised from its initially adsorbed state to a higher energy level. While the process proposed by Lennard-Jones may occur in some instances, it cannot be a general one. For this hypothesis requires that the amount of adsorption be initially proportional to the square root of the time, a relation which rarely fits time–adsorption data. Further, such a picture is unable to account for the identity of the rates of adsorption of hydrogen and deuterium on the catalysts mentioned previously.

Summary

Experiments are reported which indicate that: (1) carbon monoxide is decomposed in the sense of the equation, $2CO \longrightarrow C + CO_2$, on surfaces of zinc oxide at temperatures above 184°. (2) Carbon deposited on the catalyst is removed by hydrogen at temperatures of 184° and above, presumably as methane.

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(8) Pace and Taylor, *J. Chem. Phys.*, **2**, 578 (1934).

(9) Kohlschuetter, *Z. physik. Chem.*, **A170**, 300 (1934).

(10) Burwell and Taylor, This Journal, **58**, 697 (1936).

(11) Garner and Veal, *J. Chem. Soc.*, 1487 (1935).

(12) Ward, *Proc. Roy. Soc.* (London), **A133**, 522 (1931).

(13) Lennard-Jones, *Trans. Faraday Soc.*, **28**, 333 (1932).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

The Calculation of Second Order Reaction Velocity Constants

BY JULIAN M. STURTEVANT

Introduction.—In the application of physical methods to the determination of reaction velocities the observed quantity is usually a property of the reacting system which varies linearly with the concentrations of the reactants and products. To evaluate the two constants involved in this linear relation it is, in general, necessary to obtain the values of the observed property at the start and finish of the reaction. In many cases it is impossible to obtain these values reliably; for example, if the reaction is being followed by observation of the temperature changes resulting from the heat evolved in the system under adiabatic conditions, there would obviously be serious experimental difficulties in obtaining the temperature of the system at the completion of the reaction.

A method of calculation which eliminates these difficulties in certain cases has been described by Roseveare.[1] This method involves the analytical or graphical elimination of the "infinity reading." As pointed out by Roseveare, this method has the further advantage of not giving undue weight to the infinity reading in cases where it cannot be obtained with any greater accuracy than the other readings. Roseveare discussed the application of the method to first order reactions and to second order reactions in which the initial concentrations of the reactants are equal.

In extending the method to more complicated reactions one finds that the algebraic treatment becomes excessively cumbersome. In the present communication it will be shown that these difficulties are avoided by a simple application of the methods of projective geometry. In the course of this treatment there will be developed a very easily applied test as to whether a given set of

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(1) Roseveare, This Journal, **53**, 1651 (1931).