[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Photoiodination of the Butenes, Propylene and Ethylene at Low Temperatures. Preparation and Photolysis of 1,2-Diiodobutane

BY GEORGE S. FORBES AND ARTHUR F. NELSON

Before undertaking the experiments described below, we had attempted to follow the photobromination of butenes in liquid dichlorodifluoromethane (freon). As the thermal reaction was complete within a few minutes, even at $-150°$, we substituted iodine monobromide, but the combined bromine still reacted rapidly. The resulting purple solution, stable in the dark, slowly became colorless when irradiated at $-150°$ with a tungsten lamp.[1] Starting next with iodine and excess of butene under the same conditions, the iodine disappeared as before, but reappeared quickly upon exposure to a spark between tungsten steel electrodes.[1] Both the photoiodination of olefins and the photolysis of olefin iodides can thus be studied without interference from competing thermal reactions. At $-55°$ in chloroform, where the solubility of iodine is greater than in freon, the situation was found to be even more favorable.

DeRight and Wiig[2] have reported that iodine reacts rapidly with ethylene in carbon tetrachloride when exposed to a tungsten lamp behind a red filter having maximum transmission at λ 700 mμ. The possibility thus indicated, that the iodination can proceed through excited iodine molecules, without participation of iodine atoms, deserves further investigation.

Materials.—All samples of olefins, ethylene excepted, had been prepared in a state of exceptional purity by Professor G. B. Kistiakowsky and co-workers.[3] We are greatly indebted to them for their coöperation. The bulbs, provided with capillary inner seals and free from air, had been stored at 0°. We distilled each butene in a vacuum into a new container provided with several capillary inner seals, so that successive samples could be withdrawn without introduction of air. The propylene was condensed to a liquid, and the first portion to vaporize was discarded. A sample of commercial ethylene known to be very pure[4] was drawn from a steel cylinder and similarly treated.

Chloroform of "analytical" grade was shaken once with 9 M sulfuric acid, and the alcohol extracted by five washings with water. A treatment with aniline eliminated phosgene. The product was distilled from an all-glass Podbielniak still[5] having a 150-cm. column and a spiral of nichrome wire as packing. The reflux ratio exceeded 5, and the range was not over 0.02°.

Iodine of "analytical" grade, stated to be free from cyanogen and 99.97% pure, was resublimed from iodide and preserved in a desiccator without grease.

Apparatus and Procedure.—The reaction cell was a rectangular prism of thin fused quartz 1 × 2 cm. in horizontal cross section and 5 cm. high. It had a cylindrical neck 7 cm. long and 2 cm. in diameter. The hollow ground-glass stopper was surmounted by tubes to admit a small high-speed stirrer and to deliver or pump out gases. The jacket was made from a short Dewar vessel, to the top of which was cemented a cylinder of Pyrex 11 cm. high and 5 cm. in diameter. A rectangular opening was cut in this tube just large enough to admit a closed quartz cell 3 × 7 cm. having plane polished faces 0.5 cm. apart, which served as a double window. The jacket was insulated with cellulose wool, and enclosed in a wooden box having a hole corresponding to the window. The reaction cell behind the window was held at $-55 \pm 5°$ by liquid air added at suitable intervals. The outer surface of the double window was kept free from moisture by a current of warm air.

A bulb containing olefin vapor was fused to a gas buret through a three-way stopcock and the intervening space evacuated. A capillary inner seal was broken by a magnetic hammer and enough vapor drawn out over mercury to make 100 cc. of 0.01 M solution. By turning the stopcock the vapor was dissolved readily under chloroform at $-60°$ in a 100-cc. flask, and a millimole of iodine was added. The stock solution was stored, transferred and weighed without exposure to actinic light. It is shown below that the olefin iodide formed on standing was without influence upon the results.

The mercury vapor lamp,[6] monochromator and thermopile-galvanometer system[7] have been described. Before and after each photoiodination the linear thermopile was placed successively in three positions 1 mm. apart, close behind the exit slit so that the emerging beam was wholly covered. The sum of the three galvanometer deflections $\Sigma\Delta$ equaled kL, where L was the energy flux. Fifteen times during the research, uranyl oxalate was exposed in the reaction cell behind the double window, intercepting the whole of the beam. $\Sigma\Delta$ was redetermined before and after each exposure. When L had been found from the oxalate decomposed and the time, k was evaluated. Reflection corrections canceled out, quite nearly. Chatelet's extinction coefficients, ϵ, for iodine in chloroform at 18° were used at $-55°$ without change.[8] The contraction of the chloroform solutions, 20 to $-55°$, tended to counteract a possible decrease in ϵ over the same range.

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(1) Forbes and Nelson, THIS JOURNAL, **58**, 182 (1936).

(2) DeRight and Wiig, *ibid.*, **58**, 693 (1936).

(3) Kistiakowsky, Ruhoff, Smith and Vaughan, *ibid.*, **57**, 876 (1935).

(4) Kistiakowsky, Romeyn, Ruhoff, Smith and Vaughan, *ibid.*, **57**, 65 (1935).

(5) Podbielniak, *Ind. Eng. Chem., Anal. Ed.*, **5**, 119 (1930).

(6) Forbes and Heidt, THIS JOURNAL, **53**, 4349 (1931).

(7) Forbes, Heidt and Boissonnas, *ibid.*, **54**, 960 (1932).

(8) Chatelet, *Ann. chim.*, [11] **2**, 26 (1934).

On this basis less than 2% of incident light was ordinarily transmitted and the indicated correction factor never exceeded 1.07.

The photolyzed solution, also an unexposed sample weighed with equal care, were shaken separately in the dark with excess of 0.01 *N* thiosulfate. After drawing off the decolorized chloroform solutions, the water solutions were titrated back with standard iodine. The olefin iodides in the chloroform layers liberated no visible iodine in the dark at room temperature in twelve hours, but in diffused daylight a purple color appeared within a few minutes.

Data on Quantum Yields.—Table I gives quantuum yields, ϕ in terms of molecules of iodine reacting with olefin in light of λλ 436 and 546 mμ. An initial series of *cis*-butene, yielding very high values, could not be repeated, and was rejected. Initial concentrations were uniformly 0.01 *M* in olefin and in iodine. Experiments not marked (*b*) employed stock solutions described above containing some olefin iodide. Experiments (*b*) were started by weighing finely divided

TABLE I

BUTENE-1 AND IODINE

λ 436 mμ				λ 546 mμ			
t, sec.	Quanta per sec.	Molecules of iodine	Quantum yield	*t*, sec.	Quanta per sec.	Molecules of iodine	Qauntum yield
1800	1.17×10^{15}	4.47×10^{18}	2.09^a	1920	2.46×10^{15}	3.28×10^{18}	0.69
1800	1.18×10^{15}	4.37×10^{18}	2.04^a	1800	2.58×10^{15}	3.29×10^{18}	.71
1800	1.53×10^{15}	6.18×10^{18}	2.27	1800	2.62×10^{15}	3.34×10^{18}	.71
1800	1.54×10^{15}	5.64×10^{18}	2.12	1800	2.16×10^{15}	3.55×10^{18}	.92
1800	1.30×10^{15}	5.49×10^{18}	2.35	1800	1.99×10^{15}	3.36×10^{18}	.94
1800	1.31×10^{15}	4.58×10^{18}	1.94^b			Average	0.80
1800	1.35×10^{15}	5.67×10^{18}	2.32^b				
3600	1.46×10^{15}	9.33×10^{18}	1.78				
3600	1.46×10^{15}	9.49×10^{18}	1.81				
		Average	2.08				
			trans-Butene and Iodine				
3600	1.35×10^{15}	2.99×10^{18}	0.61	1800	2.55×10^{15}	1.68×10^{18}	0.37
3600	1.29×10^{15}	3.42×10^{18}	.73	1800	2.58×10^{15}	1.65×10^{18}	.36
3600	1.49×10^{15}	2.72×10^{18}	.51	1800	2.57×10^{15}	1.67×10^{18}	.36
3600	1.50×10^{15}	3.48×10^{18}	.65	1800	2.25×10^{15}	1.62×10^{18}	.40
				1800	2.16×10^{15}	1.41×10^{18}	.36
		Average	0.63				
						Average	0.37
			i-Butene and Iodine				
3600	1.60×10^{15}	2.66×10^{18}	0.52	3600	2.58×10^{15}	4.72×10^{18}	0.51
3600	1.59×10^{15}	2.85×10^{18}	.56	3600	2.66×10^{15}	3.89×10^{18}	.41
3600	1.62×10^{15}	2.98×10^{18}	.57	3600	2.88×10^{15}	3.88×10^{18}	.37
1800	1.52×10^{15}	1.64×10^{18}	.66	3600	2.84×10^{15}	3.58×10^{18}	.35
1800	1.57×10^{15}	1.42×10^{18}	.57			Average	0.41
		Average	0.58				
			cis-Butene and Iodine				
1800	1.62×10^{15}	7.80×10^{18}	2.67	1800	3.10×10^{15}	5.86×10^{18}	1.05
1800	1.57×10^{15}	6.96×10^{18}	2.46	1800	3.15×10^{15}	6.30×10^{18}	1.11
1800	1.56×10^{15}	6.42×10^{18}	2.28	1800	3.17×10^{15}	4.91×10^{18}	0.86
1800	1.55×10^{15}	6.73×10^{18}	2.41	1800	3.24×10^{15}	7.06×10^{18}	1.21
		Average	2.48			Average	1.06
			Propylene and Iodine				
1800	1.26×10^{15}	5.73×10^{18}	2.51^a	1800	1.96×10^{15}	2.72×10^{18}	0.77^a
1800	1.11×10^{15}	5.52×10^{18}	2.76^a	1800	1.91×10^{15}	3.71×10^{18}	1.08^a
1800	1.54×10^{15}	7.70×10^{18}	2.89	1800	2.18×10^{15}	3.67×10^{18}	0.94
1800	1.52×10^{15}	8.75×10^{18}	3.08	1800	2.23×10^{15}	3.74×10^{18}	.93
1800	1.53×10^{15}	9.07×10^{18}	3.30	1800	2.14×10^{15}	3.53×10^{18}	.92
1800	1.52×10^{15}	8.10×10^{18}	2.82	1800	2.02×10^{15}	3.35×10^{18}	.92
1800	1.31×10^{15}	6.67×10^{18}	2.84^c			Average	0.93
1800	1.33×10^{15}	5.25×10^{18}	2.19^c				
		Average	2.80				

iodine into olefin solution in the cell at −60° in the dark, so that no olefin iodide was present at the start. As such a variation in procedure had no visible effect upon ϕ, it was concluded that the iodine-sensitized photodecomposition of the olefin iodides was negligible at −60°. According to Schumacher and Wiig[9] this reaction, rapid at 100°, becomes unimportant at 20°, so that our finding is consistent with theirs. Olefin iodide does not itself absorb light perceptibly unless $\lambda < 360$ mμ.[10]

Oxygen reacts photochemically with methylene iodide[11] and accelerates the photolysis of iodoform.[12] Emschwiller[13] reports that in ultraviolet light CH_3CHI_2 and CH_2CI_2 react completely with atmospheric oxygen, while $(CHI)_2$ and $(CH_2I)_2$ are unaffected. Though we believed that our addition product was symmetrical[14] the effect of oxygen on certain photohalogenations[15] suggested caution. DeRight and Wiig froze, pumped out and melted their solutions, of ethylene and iodine, twice before exposing them to red light. In experiments marked (*c*) we carried out the above cycle three times; the solution was photolyzed in a vacuum and shaking was substituted for stirring. In experiments marked (*a*) oxygen was partially removed by bubbling gaseous freon through the cell during photolysis. The results appeared to be the same whether oxygen was removed almost completely, partially, or not at all.

Professor E. O. Wiig kindly lent his approval to our suggestion that we compare ethylene with propylene and butenes. Our procedure remained unchanged. To our surprise the total reaction after one hour scarcely exceeded the probable error of analysis. With ethylene iodide absent at the start, but without exclusion of air

λ 436 ϕ = 0.07 0.10
λ 546 ϕ = 0.00 0.03

Starting with a solution containing ethylene iodide, and without exclusion of air

λ 436 small increase in free iodine
λ 546 ϕ = 0.06 0.06 0.04
λ 577 ϕ < 0.01
λ 644 ϕ (red line of cadmium spark[16,17]) ϕ = 0.01

To decide whether the low value of ϕ at λ 644 was peculiar to the ethylene, *cis*-butene was substituted, with similar results

λ 644 ϕ = 0.01 0.02

To correlate our single experiment at λ 644 with those of DeRight and Wiig, we determined the spectral transmission of a sheet of red cellophane, and the spectral energy distribution of a 200-watt tungsten lamp, including all the infra-red. Using these data together with the energy consumption of two such lamps, and the dimensions of the apparatus, we calculated that 3.3×10^7 ergs/sec. of radiation λ 800 to 546 mμ, entered our reaction mixture. In two hours about 2.0×10^{19} molecules of iodine disappeared.

Two experiments were performed without removal of oxygen: at −55 ± 5°, $\phi = 0.007$; at 25°, $\phi = 0.004$. Also two experiments at −55 ± 5°, after removal of air by freezing, pumping and melting three times, gave 0.006 and 0.005, respectively. As DeRight and Wiig state that ethylene and iodine react rapidly in red light, it is evident that their light flux was considerably greater than ours.

The reaction scheme of Schumacher[18] has proved adequate for the discussion of previous results, photochemical as well as thermal, at room temperature.

$$I_2 + h\nu \longrightarrow I + I \qquad (1)$$
$$I + C_2H_4 \longrightarrow C_2H_4I \qquad (2)$$
$$C_2H_4I \longrightarrow C_2H_4 + I \qquad (3)$$
$$C_2H_4I + I_2 \longrightarrow C_2H_4I_2 + I \qquad (4)$$

It permits ϕ to exceed 2 (*e. g.*, *cis*-butene), and is not incompatible with small values of ϕ (*e. g.*, ethylene). We could discover no correlation between ϕ (at λ 546 and −55.0°) and $\Delta F°$ at 25° for the olefins[19] as a whole. Apparently, then, ϕ does not depend upon the stability of the olefin as a whole, as it would if stability influenced the position of equilibrium in a partial reaction involving olefin. The same holds for ϕ in its relation to the stabilities of the ethylenic linkages considered separately.[20]

To test further the adequacy of Schumacher's reaction scheme at −55°, concentrations and light intensities were varied. Owing to the labor involved, *cis*-butene alone was thus investigated. Little variation in iodine concentration was practicable. A 0.01-molar solution at −55° is nearly saturated, while light transmission and

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(9) Schumacher and Wiig, *Z. physik. Chem.*, **B11**, 47 (1930).

(10) *Cf.* DeRight and Wiig, THIS JOURNAL, **57**, 2412 (1935).

(11) Gregory and Style, *Trans. Faraday Soc.*, **32**, 724 (1936).

(12) Gibson and Iredale, *ibid.*, **32**, 571 (1936).

(13) Emschwiller, *Compt. rend.*, **199**, 854 (1934).

(14) *Cf.* A. Sherman, Quimby and Sutherland, *J. Chem. Phys.*, **4**, 732 (1936).

(15) *Cf.* Willard and Daniels, THIS JOURNAL, **57**, 2240 (1935).

(16) Wiig and Kistiakowsky, *ibid.*, **54**, 1807 (1932).

(17) Forbes and Heidt, *ibid.*, **56**, 1671 (1934).

(18) Schumacher, *ibid.*, **52**, 3132 (1930).

(19) Values from Parks, *Chem. Rev.*, **18**, 325 (1936).

(20) Values from Kistiakowsky and co-workers, refs. 3, 4.

analytical errors impair results when $c < 0.005$. Experimental data appear in the first three columns of Table II, the unit of volume being one cc. In the fourth is the observed rate of disappearance of iodine in moles per second, and in the fifth the widely fluctuating rate constant calculated by inserting the photochemical formation of iodine ions into Schumacher's scheme. At −55° the expression $\mathrm{d}[BI_2]/\mathrm{d}t\,[B][I_2]L_a$ given in the last column is much more nearly constant.

TABLE II

$[B] \times 10^6$	$[I_2] \times 10^6$	L_a (Einsteins/cc.) $\times 10^{10}$	$-\frac{\mathrm{d}[I_2]}{\mathrm{d}t} \times 10^{10}$	$\frac{\mathrm{d}[BI_2]}{\mathrm{d}t} \Big/ [B]\sqrt{L_a}$	$\frac{\mathrm{d}[BI_2]}{\mathrm{d}t} \Big/ [B][I_2]L_a \times 10^{-10}$
4.57	9.62	1.88	2.18	3.48	2.61
4.55	9.60	1.98	2.14	3.35	2.47
4.54	9.59	2.18	1.99	2.94	2.10
6.67	10.18	1.54	3.88	4.70	3.71
6.74	10.25	1.50	3.32	4.02	3,20
6.67	10.18	1.45	3.88	4.84	3.94
8.12	7.64	2.68	7.15	5.38	4.30
8.09	7.61	2.60	6.40	4.90	4.00
8.05	7.57	2.58	5.88	4.55	3.74
8.00	7.52	2.56	6.17	4.81	4.00
35.35	5.60	2.06	16.75	3.48	4.10
35.18	5.43	1.95	15.44	3.13	4.15
35.04	5.29	2.08	17.23	3.41	4.47
10.00	4.52	1.12	1.57	1.49	3.10
9.90	4.42	1.12	1.67	1.58	3.40
9.88	4.40	1.10	1.72	1.64	3.60
9.40	8.86	0.328	0.86	1.58	3.14
9.33	8.79	.259	.52	1.11	2.45
8.99	6.49	.756	1.14	1.11	2.59
8.96	6.46	.754	1.23	1.20	2.82
19.38	8.63	.292	1.17	1.11	2.40
19.52	8.78	.276	1.19	1.17	2.51
50.66	7.64	.209	1.99	0.85	2.41
49.60	6.60	.178	1.89	0.88	3.24
49.13	6.13	1.19	10.21	1.90	2.84
49.10	6.00	1.23	9.97	1.84	2.75

Preparation and Photolysis of 1,2-Diiodobutane.—A solution of iodine with excess of butene-1 in freon at −70° was illuminated by two gas-filled tungsten lamps through liter beakers filled with water and serving as lenses until the solution became colorless. The freon was evaporated under reduced pressure below its boiling point, −29.8°, carrying off the excess of butene (b. p. −6°). The white crystals, only about 10 mg. in weight, could not be purified readily by recrystallization, but were believed to be mainly the symmetrical compound.[14] After drying below −25° for several hours, the melting point was −15 ± 1°; the oily liquid was stable at −15° in the dark for some time, but iodine was liberated promptly upon exposure to diffused daylight. A microanalysis of the compound was performed in Converse Laboratory: found 15.56 and 16.49% of C, also 2.84 and 2.94% of H. Calculated for $C_4H_8I_2$, 15.48% of C and 2.60% of H.

We prepared 2,3-diiodobutane in similar fashion from butene-2 (*trans*) also as a white solid. This melted at −11 ± 2° with immediate decomposition, so that attempts at analysis were unsuccessful.

The quantum yield for photolysis of 1,2-diiodobutane in light of λ 254 was determined, using a special argon-filled quartz mercury vapor lamp ("Fluorolight"). As we found 77% of the whole to be resonance radiation,[21] we dispensed with the monochromator. The solution of 1,2-diiodobutane, prepared as above, was slightly purple at the start. The quantum yields appear in Table III under the assumption that diiodobutane absorbed all the resonance radiation. DeRight and Wiig[10] found that ethylene iodide began to absorb at λ 360 and absorbed strongly at λ 313. No allowance was made for absorption by the iodine, since at its mean concentration it could have absorbed only 12% of the incident light even if the strongly absorbing diiodobutane had been absent.

TABLE III

QUANTUM YIELDS OF PHOTODECOMPOSITION OF 1,2-DIIODOBUTANE

T, °C.	t, sec.	Quanta per sec. $\times 10^{-14}$	Molecules decomposed $\times 10^{-18}$	Quantum yield
−55	3600	10.6	2.7	0.7
−55	3600	10.1	2.4	.65
−55	3600	12.2	3.5	.75
−20	3600	12.1	4.1	.95
−20	3600	11.4	4.3	1.05
24	2400	11.4	3.1	1.15
25	2400	11.5	3.1	1.15
25	3600	12.6	4.9	1.1

DeRight and Wiig[10] (p. 2414) have reported for ethylene iodide at room temperature ϕ = 0.71, 0.74, 0.75, 0.81, 0.81. We calculate 1.06 as the ten-degree temperature coefficient from ϕ at −55 and at 25°. From ϕ at −55 and −20° we find 1.08.

We are indebted to the du Pont Fund of the Division of Chemistry for a part of the apparatus used in this investigation.

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[21] *Cf.* W. G. and P. A. Leighton, *J. Chem. Ed.*, **12**, 139 (1935).

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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The Adsorption and Decomposition of Carbon Monoxide on Zinc Oxide Catalysts

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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.