Anal. Calcd. for $C_{18}H_{21}ON$: N, 5.24. Found: N, 5.20.

This higher melting substance was converted into 4,4′-dihydroxy-α,α'-diethylstilbene as follows: A solution of 50 mg. of it in dilute sulfuric acid was diazotized with sodium nitrite in the usual manner. To this solution 10 ml. of 18 *N* sulfuric acid was added and the resulting solution was refluxed for half an hour. The crude material obtained was recrystallized from dilute methanol; yield 0.013 g.; m. p. 169.5–170.5°. This substance mixed with authentic *trans* 4,4′-dihydroxy-α,α'-diethylstilbene showed no depression of the melting point.

Thus it appears that the recently isolated higher melting substance is the *trans* isomer and that the previously described lower melting substance was probably the *cis* isomer.

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Physical Adsorption from Mixtures of Gases. II. Oxygen–Argon on Silica Gel at 0°[1]

BY LOCKE WHITE, JR., AND CHARLES H. SCHNEIDER

Lambert and Heaven[2] have reported experiments which led to the conclusion that, in adsorption from binary mixtures by silica gel at 0°, "the composition of the adsorbed phase is greatly affected by the order in which the two gases reach the gel surface." In their apparatus, the gaseous mixture was not circulated through the bed of adsorbent and the rate of approach to equilibrium was presumably limited by diffusion; however, their diffusion paths were short and they allowed very long periods for the attainment of equilibrium. In view of the unexpected nature of their results, it seemed worthwhile to repeat some of their measurements, using forced circulation.

Experimental

Apparatus and Materials.—The apparatus was that of a previous investigation.[3] For this use, an ice-bath was substituted for the temperature-control system described. Gas analysis was accomplished by readings of total pressure on a manometer and of partial pressure of oxygen by Pauling's magnetic device.[4] Oxygen, argon and helium (for calibrating the dead space in the sample cell) were prepared by the procedures used previously.[3]

Lambert and Heaven used a sample[5] from the Silica Gel Corporation of America. This company is no longer in existence, having been taken over by the Davison Chemical Corporation, which has no record of the sample supplied to Lambert and Heaven, but which contributed a sample of its 14–20 mesh silica gel, grade code 08, for this investigation. Approximately 40 g. was used.

Procedure.—Before each measurement, the surface of the sample was cleaned by evacuation to less than 10^{-3} mm. of mercury at 150° for at least an hour. After the sample was cooled to 0°, a measured quantity of one component was added and allowed to equilibrate, and the pressure was recorded. Then an approximately equal quantity (±2%) of the other component was added and allowed to equilibrate, and both total pressure and partial pressure of oxygen were recorded. The surface of the sample was then cleaned and the procedure was repeated, except that the components were added in the reverse order. A pair of such runs was ordinarily made each day.

To avoid the possibility that a regular pattern as to which gas was added first was giving deceptive results, an extra pair of runs (nos. 9 and 10 in Table I) was made with the daily pattern reversed.

In none of the first ten runs was there any attempt to "wash out" the gel in the manner which Lambert and Heaven found to be essential for reproducibility. In run no. 11, on the contrary, the "washing out" was performed. That is, an unmeasured quantity of argon was adsorbed to equilibrium on the clean surface at 0° and was then removed by heating and evacuation. Another unmeasured quantity was similarly adsorbed and removed. Then the adsorption of argon was measured in the usual way.

Results

The adsorption data obtained are recorded in Table I. Because no data have been omitted, it is possible to tell from the table which adsorbate was in contact with the gel immediately preceding any run under consideration.

TABLE I

ADSORPTION DATA

Run	Oxygen Volume ads., ml. at S. T. P.	Oxygen Pressure, mm. Obs.	Oxygen Pressure, mm. Calcd.	Argon Volume ads., ml. at S. T. P.	Argon Pressure, mm. Obs.	Argon Pressure, mm. Calcd.
1	5.77	42.0	42.4	...	...	...
	5.23	40.0	38.4	5.40	40.5	39.2
2	...	...	...	5.88	42.5	42.7
	5.35	40.0	39.3	5.43	38.5	39.4
3	10.33	75.5	75.9	...	...	...
	10.31	76.0	75.8	10.11	72.5	73.4
4	...	...	...	10.89	78.0	79.1
	10.37	76.0	76.2	9.97	72.5	72.4
5	16.91	123.5	124.3	...	...	...
	15.50	114.0	113.9	15.73	113.0	114.2
6	...	...	...	17.04	123.0	123.7
	15.54	114.0	114.1	15.48	113.0	112.4
7	24.64	180.5	181.0	...	...	...
	22.60	166.0	166.1	22.67	166.5	164.6
8	...	...	...	24.72	179.5	179.5
	22.80	166.0	167.6	22.62	166.5	164.2
9	...	...	...	20.61	149.0	149.2
	19.19	142.0	141.0	18.89	137.5	137.1
10	20.91	154.0	153.7	...	...	...
	19.14	142.0	140.7	19.18	137.5	139.2
11	...	...	...	17.13	123.5	124.4

The measured points of each run, whether for oxygen or for argon, are so nearly superposed that it is impractical to distinguish between them on a graph. To show how nearly the volume

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(1) This research was supported jointly by the Office of Naval Research and the Institute-Sponsored Research Fund of Southern Research Institute.

(2) B. Lambert and H. S. Heaven, *Proc. Roy. Soc.* (*London*), **A153**, 584 (1936).

(3) L. White and C. H. Schneider, THIS JOURNAL, **71**, 2593 (1949).

(4) L. Pauling, R. E. Wood and J. H. Sturdivant, *ibid.*, **68**, 795 (1946).

(5) B. Lambert and A. M. Clark, *Proc. Roy. Soc.* (*London*), **A117**, 183 (1927)

of either component adsorbed is a linear function of its partial pressure, independent of the presence or absence of the other component, the two best lines showing this relationship were calculated by the method of least squares. In the equation $p = aV$ in which p is the partial pressure and V is the volume adsorbed, the constant a is 7.35 for oxygen and 7.26 for argon. (Pressure has been taken as the dependent variable for consistency with the graphs of Lambert and Heaven.) The pressures calculated from these equations are included in the table. In evaluating the data, it should be considered that the rated accuracy of the oxygen analyzer is ± 1% of full scale, or ± 2.3 mm.

As an additional characterization of the sample used, an adsorption–desorption isotherm for oxygen on 0.82 g. at −194.6° is shown in Fig. 1.

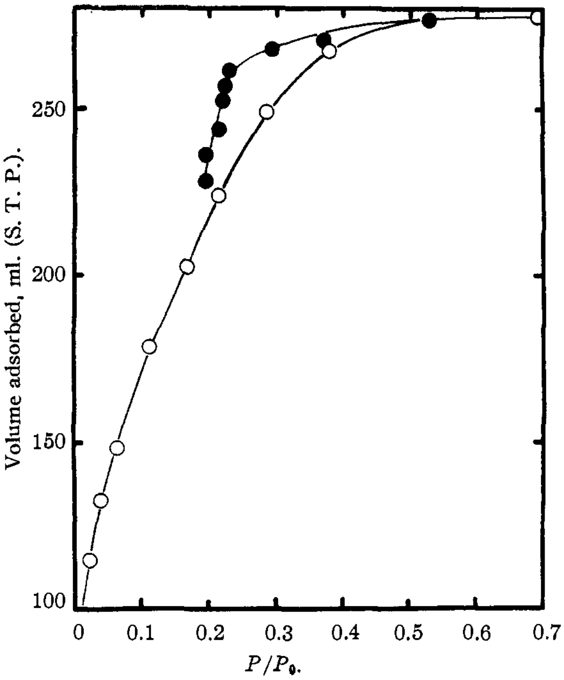

Fig. 1.—Adsorption–desorption isotherm for oxygen at −194.6°: ○, adsorption; ●, desorption.

With forced circulation of oxygen–argon mixtures through the sample used here, it is certainly not true that "the composition of the adsorbed phase is greatly affected by the order in which the two gases reach the gel surface." Unless there are vital differences between the sample used here and that of Lambert and Heaven it must be concluded that their results represented a pseudo-equilibrium, attributable to the slowness of diffusion.

The "washing out" procedure which Lambert and Heaven found to be prerequisite to reproducibility had no effect here. This is shown by the reproducibility and reversibility obtained in most of the runs without "washing out," and by the complete absence of any change in run no. 11, when it was used.

SOUTHERN RESEARCH INSTITUTE
BIRMINGHAM, ALABAMA RECEIVED JANUARY 24, 1949

The Reduction of Phenanthridine by Lithium Aluminum Hydride

BY W. C. WOOTEN[1] AND R. L. MCKEE

Lithium aluminum hydride has been found to convert phenanthridine into 5,6-dihydrophenanthridine in boiling ether in a molar ratio of 1:2.5. The reduction did not proceed beyond the dihydro stage with a larger excess of hydride (molar ratio of 1:1) under the conditions employed. Addition of the hydride to phenanthridine in boiling ether likewise gave a comparable yield of 5,6-dihydrophenanthridine.

Experimental

Forty grams (0.22 mole) of phenanthridine was introduced by use of a Soxhlet extractor into a well-stirred solution of 3.2 g. (0.087 mole) of lithium aluminum hydride in 500 cc. of anhydrous ether over a period of ten hours. The excess hydride was destroyed by addition of wet ether after which a solution of 70 cc. of hydrochloric acid in 500 cc. of water was added. It was necessary to filter at this stage to remove precipitated dihydrophenanthridine hydrochloride. The ether layer was discarded and the solid hydrochloride was combined with the aqueous solution and made strongly basic (sodium hydroxide). The product was extracted four times with a total of 1100 cc. of ether. The resulting solution was dried (magnesium sulfate) and the ether distilled. A single recrystallization from petroleum ether afforded 32.5 g. of material melting at 123–125°. A second crystallization yielded 30 g. (74%) of 5,6-dihydrophenanthridine. The melting point of this product was 123.5–124.5°, at variance with the value reported by Pictet and Ankersmit[2] but in agreement with recent workers.[3]

Anal. Calcd. for $C_{13}H_{11}N$: C, 86.16; H, 6.12; N, 7.73. Found: C, 86.01; H, 6.12; N, 7.61.

Treatment of the dihydro compound in pyridine with benzoyl chloride formed the 5-benzoyl derivative, m. p. 90.5–92.5°.

Anal. Calcd. for $C_{20}H_{15}NO$: N, 4.91. Found: N, 4.97.

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[1] Tennessee Eastman Corporation Fellow.

[2] Pictet and Ankersmit, *Ann.*, **266**, 138 (1891).

[3] Diesbach and Aeschbach, *Helv. Chim. Acta*, **28**, 1392 (1945); Ritchie, *J. Proc. Roy. Soc. N. S. Wales*, **78**, 134 (1945), through *C. A.*, **40**, 876 (1946).

THE VENABLE CHEMICAL LABORATORY
THE UNIVERSITY OF NORTH CAROLINA
CHAPEL HILL, N. C. RECEIVED FEBRUARY 12, 1949

α- and β-Bromocrotonolactones

BY M. C. WHITING

In reviewing the literature concerning the stereochemistry of mono-adducts formed by acetylenic compounds, it was noticed that Lespieau and Viguier[1] obtained by the action of hydrobromic acid on γ-hydroxytetrolic acid a bromocrotonolactone, m. p. 77°, which had been

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[1] Lespieau and Viguier, *Compt. rend.*, **146**, 295 (1908); *Ann. chim.*, **27**, 178 (1912).