

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

The Adsorption of *cis*- and *trans*-Azobenzene

BY HERBERT FREUNDLICH AND WILFRIED HELLER

G. Spencer Hartley¹ has shown that commercial azobenzene mainly consisting of the *trans* isomer can be converted partly into the *cis* isomer, when exposed to daylight in dilute solution. He succeeded in separating the two isomers and in preparing them in a pure form. A. H. Cook² and L. Zechmeister³ found that separation could be effected by adsorption, using the chromatographic method (aluminum oxide as adsorbent, petroleum ether as solvent); *cis*-azobenzene was adsorbed more strongly than the *trans* isomer.

The stronger adsorption of the *cis* compound on aluminum oxide as it is emphasized in the latter papers might lead to the presumption that *cis* isomers generally are adsorbed more strongly than *trans* isomers. Freundlich and Schikorr⁴ have found, however, that maleic acid, a *cis* compound, is adsorbed far less than the *trans* isomer, fumaric acid, in aqueous solution on charcoal. This seems to indicate that it depends on the affinity of the solute to the adsorbent and to the molecules of the solvent, whether the *cis* or the *trans* isomer is adsorbed more strongly. Taking water as a standard, as it were, one could say that the more hydrophilic or more hydrophobic nature of the adsorbent (case 1) and of the solvent (case 2) are decisive for the difference in adsorbabilities of the solutes in question. That influences of this kind have to be taken into account is shown most clearly by the adsorption of methyl violet by charcoal or silica gel in water and tetralin, respectively, investigated by E. Berl and E. Wachendorff.⁵ Dissolved in "hydrophobic" tetralin, methyl violet is adsorbed more strongly by the hydrophilic silica gel; in an aqueous solution, on the contrary, by the hydrophobic charcoal. Here we are dealing with case 2. From the outset, case 1 appears to be just as likely. In any case, the strongest contrast to the behavior of aluminum oxide in petroleum ether was to be expected with a hydrophobic adsorbent like charcoal and a hydrophilic solvent.

(1) G. Spencer Hartley, *Nature*, **140**, 281 (1937); *J. Chem. Soc.*, 633 (1938).

(2) A. H. Cook, *ibid.*, 876 (1938).

(3) L. Zechmeister, O. Frehden and P. Fischer Jörgens, *Naturwissenschaften*, **26**, 495 (1938).

(4) H. Freundlich and G. Schikorr, *Kolloid-Beihfte*, **22**, 1 (1926).

(5) E. Berl and E. Wachendorff, "Zsigmondy-Festschrift," 36 (1925), Spec. No. of *Kolloid-Z.*, **36** (1925).

We prepared *cis*-azobenzene by somewhat modifying Hartley's method. We avoided vacuum distillation and the tedious fractionating by crystallization; instead of that, we separated the two isomers by the differences in their solubilities in water and purified the *cis* compound by crystallization from petroleum ether at low temperatures (-15 to -35°). The m. p. of our crystals was 71.7° , determined by quick plunging; Hartley's value is 71.4° , Cook's 71° .

trans-Azobenzene was prepared following Hartley's method.

Methyl alcohol was chosen as hydrophilic medium, petroleum ether as the hydrophobic one; aluminum oxide was the hydrophilic adsorbent, charcoal (Norit) the hydrophobic one. The adsorption experiments were done at 20° . Five cc. of solution was shaken with different amounts of adsorbent for a few minutes, until the final state of adsorption was reached. The adsorbent was then separated from the solution by centrifuging; this lasted five to ten minutes in solutions of petroleum ether (b. p. 55 to 65°), fifteen to twenty minutes with methyl alcohol. We started with a 0.5% solution and reached different final concentrations by varying the amount of adsorbent. This procedure may lead to irregularities in adsorption, when small amounts of adsorbent (below 0.1 g.) are used (this refers to two measurements at higher concentrations of the *trans* isomer not taken into account in Fig. 2; cf. also H. Morawitz⁶).

The concentration after adsorption was determined with a colorimeter, using standard solutions of the same isomer as comparison. In the experiments with the *cis* isomer both standard solutions and those used for adsorption were freshly prepared every thirty minutes. Light-filters were used. A small amount of adsorbent, remaining in suspension, then became noticeable by a change in absorption, when passing from blue to red, namely, by requiring different values of the layer thickness for which equality of the half-shades was observed. Samples behaving in this way were rejected.

All operations were carried out in the dark or in indirect red light. The light intensity of the

(6) H. Morawitz, *Kolloid-Beihfte*, **1**, 301 (1910).

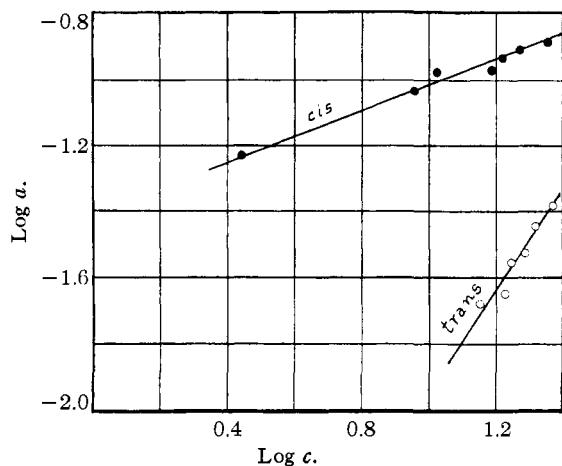


Fig. 1.—Adsorption of *cis*- and *trans*-azobenzene by aluminum oxide in petroleum ether: c in millimoles per liter, a in millimoles per 1 g. of adsorbent.

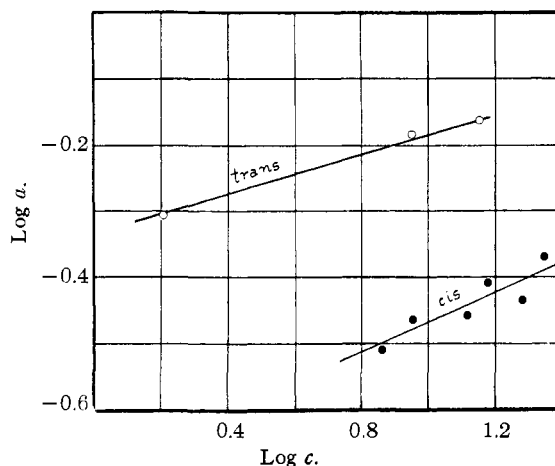


Fig. 2.—Adsorption of *cis*- and *trans*-azobenzene by charcoal in methyl alcohol: c in millimoles per liter, a in millimoles per 1 g. of adsorbent.

colorimeter was kept weak enough to prevent a noticeable *cis-trans* transformation during two minutes of illumination; the actual illumination lasted 8 times five seconds during one experiment.

The results obtained with aluminum oxide in petroleum ether and with charcoal in methyl alcohol are given in Figs. 1 and 2. c is the equilibrium concentration in millimoles per liter, a is the amount adsorbed in millimoles per 1 g. of adsorbent. The adsorption isotherms are represented in a logarithmic diagram showing that the empirical equation $a = ac^{1/n}$ holds fairly well. In the case of the weak adsorption of the *trans* isomer by aluminum oxide in petroleum ether $1/n$ is practically about 1; in the other cases it lies between 0.30 and 0.45, *i. e.*, it agrees with the values generally found.

In agreement with Cook's chromatographic experiments, Fig. 1 proves that the *cis* isomer is adsorbed much more strongly than the *trans* isomer by aluminum oxide in petroleum ether. In agreement with our expectations, the behavior is reversed with charcoal as adsorbent in methyl alcohol (*cf.* Fig. 2). On comparing the values of a for an equilibrium concentration of 10 millimoles per liter, we find

$$\begin{aligned} a \text{ (} cis \text{; aluminum oxide, petroleum ether)} &= 0.093 \\ a \text{ (} trans \text{; aluminum oxide, petroleum ether)} &= 0.012 \\ a \text{ (} cis \text{; charcoal, methyl alcohol)} &= 0.34 \\ a \text{ (} trans \text{; charcoal, methyl alcohol)} &= 0.65 \end{aligned}$$

Some adsorption experiments were done with aluminum oxide in methyl alcohol and with charcoal in petroleum ether. As was to be expected, the difference in the behavior of the azobenzene

isomers was somewhat less pronounced. Again comparing the a -values for an equilibrium concentration of 10 millimoles per liter, we found

$$\begin{aligned} a \text{ (} cis \text{; aluminum oxide, methyl alcohol)} &\text{ about } 0.004 \\ a \text{ (} trans \text{; aluminum oxide, methyl alcohol)} &\text{ about } 0.002 \\ a \text{ (} cis \text{; charcoal, petroleum ether)} &= 0.43 \\ a \text{ (} trans \text{; charcoal, petroleum ether)} &= 0.58 \end{aligned}$$

It was always observed that $1/n$ was larger for the solute which is adsorbed less, independent of the nature of the solvent; this is seen from the two figures and it was also very marked in the adsorption by charcoal in petroleum ether. At higher concentrations the lines of the adsorption isotherms (in the logarithmic diagram) would intersect, provided that the whole behavior is not changed by the occurrence of saturation.

In our experiments the influence of the more hydrophilic or more hydrophobic nature of the adsorbent prevails (case 1), the succession of the adsorbents is the same in both media, in contrast to the experiments with methyl violet, mentioned above. But there is also in our case an influence of the solvents in the same direction, as is shown when the differences in the amounts adsorbed are compared.

Adsorption experiments with another hydrophilic adsorbent, namely, powdered silica gel, again showed that *cis*-azobenzene is more strongly adsorbed in petroleum ether than the *trans* isomer. The difference is markedly smaller than with aluminum oxide.

Our results agree with the fact, mentioned above, that fumaric acid, the *trans* isomer, is adsorbed more strongly than maleic acid by char-

coal in water; for an equilibrium concentration of 10 millimoles per liter we have (Freundlich and Schikorr): a (maleic acid) = 0.992; a (fumaric acid) = 1.56.

The more hydrophilic nature of *cis*-azobenzene compared with the *trans* compound also is indicated in the differences of solubilities. According to Hartley the solubility (at 25°) of the *cis* isomer in water is 0.65 millimole per liter, that of the *trans* isomer 0.02 millimole per liter in petroleum ether (b. p. 40 to 60°); on the other hand, the *cis* isomer is less soluble (at 0°), 49.4 millimoles per liter, compared to a value of 192 for the *trans* isomer. We determined colorimetrically the solubilities in methyl alcohol at 0° and found a succession as in water: 410 millimoles per liter for *cis*-azobenzene, 164 for the *trans* isomer.

It is quite probable that the *cis* isomers are generally more hydrophilic than the *trans* isomers. Perhaps it is due to a *cis-trans* difference in structure that maltose is more hydrophilic than cellobiose—as it appears to be—and accordingly starch so much more hydrophilic than cellulose.

Summary

The adsorptions of pure *cis*- and *trans*-azobenzene by aluminum oxide and by charcoal in solutions of petroleum ether and of methyl alcohol were measured and compared. The *cis* isomer is adsorbed more strongly by aluminum oxide, particularly in petroleum ether, less in methyl alcohol; the *trans* isomer is adsorbed more strongly by charcoal, particularly in methyl alcohol, less in petroleum ether. This is in agreement with other experimental results, according to which the more hydrophilic solute, here the *cis* isomer, is adsorbed more strongly by a hydrophilic adsorbent, here aluminum oxide, in a more hydrophobic medium, here petroleum ether, than by a more hydrophobic adsorbent, here charcoal, in a more hydrophilic medium, here methyl alcohol.

That *cis*-azobenzene is more hydrophilic than *trans*-azobenzene is also shown by the *cis* isomer being more strongly soluble in water and methyl alcohol and less soluble in petroleum ether than the *trans* isomer.

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Homogeneous Catalytic Hydrogenation

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Last year it was announced¹ that quinone in quinoline solution could be hydrogenated using dissolved cuprous acetate as homogeneous catalyst. This is a report of further study of the kinetics of this reaction in the attempt to discover precisely what structure has this important property of bringing the highly inert hydrogen molecule into reaction.

Experimental

The apparatus was essentially the same as already has been mentioned,¹ and the experiments consisted of following the rate at which hydrogen was absorbed by a given solution varying the conditions of concentration, solvent, temperature, and reactants. The detail of the reaction vessel is shown in Fig. 1. The internal condenser was removed and weighed amounts of the catalyst and substrate introduced. The vessel was then mounted in the shaker and connected to the vacuum system through the ground joint J. The solvent was run in from a pipet and the condenser quickly replaced and the tap to the vacuum system opened. But before the air could be removed some oxidation had taken place, so that blank runs without substrate were

made on a given catalyst to determine the correction to be applied to the amount of hydrogen absorbed. The heating was then commenced and pumping was continued until the McLeod gage at the other end of the system showed a pressure of 10^{-4} mm. or less. This degassing sometimes took as long as thirty minutes after the thermostating liquid had reached its boiling point. For runs at 100° water was used and for 117.7° *n*-butyl alcohol was used as thermostating liquid. In all the runs the shaker speed was about 325 vibrations per minute. In the course of one run the shaker speed was increased to 530 vibrations per minute for a time and then decreased to 325 again and no appreciable break in the rate curve was observed, showing that the rate of solution of the gas was sufficiently fast not to be a disturbing factor.

Materials

Quinoline.—Eastman Kodak Co. synthetic quinoline was purified by (1) initial fractionation at atmospheric pressure to within 1°, (2) treatment with benzoyl chloride for several days and then washed with sodium hydroxide solutions followed by distilled water, (3) fractionation at atmospheric pressure to remove water, (4) final fractionation in a 1-foot (30-cm.) Widmer column at 50–60 mm. pressure. The quinoline so obtained remains water white for months when kept in a glass-stoppered uncolored glass bottle.

(1) M. Calvin, *Trans. Faraday Soc.*, **34**, 1181 (1938).