

setting in of free rotation around the ethylenic carbons and subsequent deactivation, the large difference in activation energy being due to: (1) in the case of isostilbene the strength of the double bond may be greater due to the presence of the phenyl groups; (2) according to Tolman the measured energy of activation represents the difference in energy of average and activated molecules. This may be very different for stilbene and ester molecules since according to Raman spectra the two possess quite different oscillation frequencies. That this could account for large differences in activation energy will be demonstrated by Rice and Gershinowitz.¹⁰

The greater similarities of vibrational frequencies of the ethylenic carbon bond and the double bonds of the attached phenyl groups may account for the efficient energy transfer in isostilbene as contrasted with the esters.

Studies now in progress on esters of *cis* and *trans* cinnamic acid as well as derivatives of stil-

(10) O. K. Rice and H. Gershinowitz, in press.

bene should yield data which will enable us to give a more comprehensive picture of the above facts.

Summary

1. Thermal isomerization of dimethyl citrate has been investigated. Although the data obtained do not allow quantitative conclusions, evidence is obtained that this reaction is very similar to the earlier described isomerization of dimethyl maleate.

2. Isomerization of isostilbene to stilbene has also been studied. This unimolecular reaction has an activation energy of 43,000 calories and shows no falling off with pressure down to 4 mm. At least 12 oscillators must participate in the isomerization process.

3. Equilibrium in the gaseous system stilbene \rightarrow isostilbene has been observed. Equilibrium constants near 600 Å. are of the order of 0.07, from which an approximate heat of reaction of 3000 calories is calculated.

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The Heat of Adsorption of Carbon Monoxide on Copper¹

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In support of the theory that the atoms in the surface of an adsorbent possess varying degrees of activity, attention has been called to the measurements of heats of adsorption made by Bull, Hall and Garner² for oxygen on charcoal and by Beebe³ for carbon monoxide on copper. In both researches it was reported that the differential heats of adsorption decreased progressively as successive small increments of gas were added to the adsorbing surface. The higher initial heats were explained by assuming that the first small portions of gas were adsorbed on atoms of charcoal, or of copper, of relatively high activity as compared to the other atoms in the surfaces.

Recently, several cases have been reported in which the differential heats of adsorption were found to be independent of the amount of gas already adsorbed on metallic surfaces.⁴ More-

over defects have been discovered⁵ in much of the earlier calorimetric work which may lead to serious errors in the results, especially for the initial stages of adsorption where the residual gas pressures are low. As a result some doubt has been cast on the reliability of the measurements for carbon monoxide on copper. One of us has reported elsewhere^{5c} a careful search for possible sources of error in this case. With the information gained by this study, a new calorimeter has been designed and the measurements have been repeated for the initial stages of the adsorption.

Experimental

Description of the Method.—For reasons to be discussed later, the method was a modification of that developed by Bull, Hall and Garner² in its final form. The glass vacuum chamber used by these authors was simplified as shown in Fig. 1. While measurements were being taken, this chamber was maintained at constant temperature by an ice-water mixture. By vacuum jacketing the reference junction, it was possible to obtain time-temperature

(1) This article is based upon experimental work done by E. L. Wildner in partial fulfillment of the requirements for the degree of Master of Arts at Amherst College.

(2) Bull, Hall and Garner, *J. Chem. Soc.*, 837 (1931).

(3) Beebe, *J. Phys. Chem.*, **30**, 1538 (1926).

(4) (a) Ward, *Proc. Roy. Soc. (London)*, **A133**, 506 (1931); (b) Garner and Kingman, *Trans. Faraday Soc.*, **27**, 322 (1931); (c) Maxted and Hassid, *ibid.*, **29**, 698 (1933).

(5) (a) Maxted and Hassid, *J. Chem. Soc.*, 3313 (1931); (b) Schwab and Brenneke, *Z. physik. Chem.*, **16B**, 19 (1932); (c) Beebe, *Trans. Faraday Soc.*, **28**, 761 (1932).

curves which were entirely smooth. A variation of 0.0002° would have been noticeable.

The calorimeter differed from the final form used in Garner's laboratory in two respects: (a) it was made of copper instead of platinum, and (b) the active copper granules were packed in thirty horizontal layers about 2 mm. thick and separated by copper gauze disks. These changes were made to improve the conditions for the rapid distribution of heat throughout the assembled calorimeter.

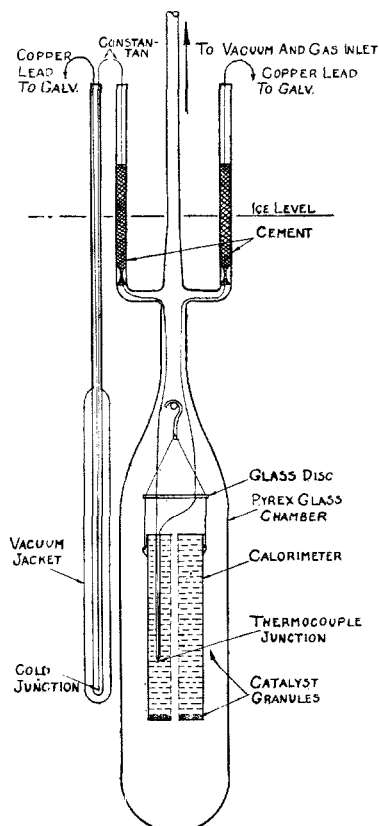


Fig. 1.

The copper-constantan thermocouple junction, whose lead wires were 0.018 cm. in diameter, was inserted into the calorimeter to a depth of 4.5 cm. The temperature changes were recorded by use of a sensitive galvanometer of seven seconds period which gave a deflection of 1 mm. per 0.00158° at a distance of 1.37 meters. The volume of the reaction train including the McLeod gage was 264 cc. Tests with helium showed the absence of any "gas effect,"^{4b} even for the highest pressures under which measurements were made.

The total weight of the assembled calorimeter was 71.5 g. (water equivalent, 6.59 calories) of which 40.0 g. was due to the active copper adsorbent. The latter, which adsorbed 2.4 cc. of carbon monoxide at 0.3 mm. pressure, was a portion of the 78-g. sample used by one of us in previous work. It had lost about 40% of its original adsorbing power. Before each series the copper was degassed at 160° . The helium, purchased from the Ohio Chemical Manufacturing Company, was guaranteed 99.9% pure.

Because it produced no heat effect when admitted to the copper surface, the authors were convinced that it had no adsorbable impurities. The carbon monoxide was prepared by dropping concentrated formic acid solution into concentrated sulfuric acid, in a previously evacuated flask. The gas was purified by passing through a train consisting of copper at 400° , solid potassium hydroxide and anhydrous magnesium perchlorate in sequence.

Discussion of the Method

It has been shown^{5c} that (a) the conduction of heat between copper grains and from the copper grains to the thermocouple junction is slow at low pressures of residual gas, and (b) the initial increments of carbon monoxide are not uniformly adsorbed but are rather adsorbed on those successive layers of active adsorbent with which the gas first comes in contact. In these respects the reaction is similar to that of oxygen on charcoal studied by Bull, Hall and Garner.² These authors have discussed in considerable detail their reasons for believing that the calorimeter developed by them has corrected the defects due to slow heat transfer and non-uniform adsorption. We shall now discuss briefly whether our modified calorimeter has been as effective in the present measurements.

Slow Conduction of Heat.—As stated in the description of the calorimeter, the distribution of heat was accelerated by use of the all-copper vessel and the copper gauze disks. In Fig. 2 are shown photographic reproductions of three typical twenty-minute time-temperature curves which

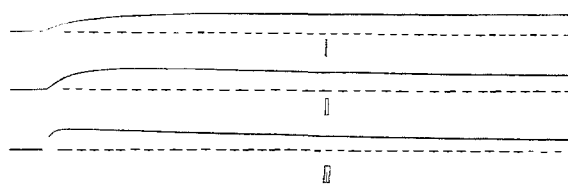


Fig. 2.

were originally photographically recorded. Dotted reference lines have been added. Curve I resulted from the addition of an initial increment of gas to a degassed surface, Curve III, from a later increment added after the residual gas pressure was about 0.3 mm. and Curve II represents an intermediate stage. In Curve I the maximum temperature was not reached until after eight minutes, but because there was no residual gas pressure, the rate of cooling was very slow. In Curve III the rate of cooling was much greater but the maximum temperature was reached in

less than one minute.⁶ Hence in all the measurements, whether for initial or later portions, the error introduced by extrapolating to zero time was very small although the calorimeter was not adiabatic.

Non-uniform Adsorption.—A non-uniform adsorption process may affect the measurements of heats in two ways, which will be called effects (a) and (b): (a) the heat is liberated in a restricted region rather than uniformly, and (b) if the surface contains atoms of different activities, then the first increments of carbon monoxide are adsorbed on copper atoms of differing degrees of activity over a limited region, rather than on the atoms of highest activity throughout the catalyst mass, or in other words, the heats measured are integral heats for successive layers of adsorbent rather than differential heats for the whole sample.

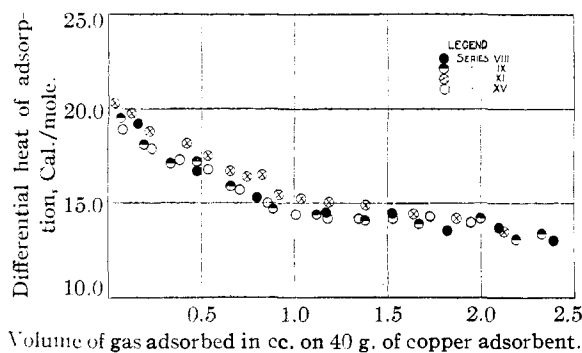


Fig. 3.

The chance of error from effect (a) has been minimized by arranging for more effective heat distribution. Effect (b) cannot be eliminated so long as the adsorption process is non-uniform. The authors are not aware that this difficulty has been considered in previous publications. Ideally, effect (b) could be eliminated only by using an adsorbent layer of infinitesimal thickness. Practically, the method used approaches the ideal condition, because the gas must enter into the center of the calorimeter and then diffuse radially through the annular layer of active copper granules. But it is very probable that the adsorption process is not entirely uniform even under these conditions. If as a consequence of the non-uniformity of the adsorption process the initial measurements in a series represent integral heats over a limited region rather than differential

(6) It should be added that the time lag in reaching the maximum temperature was due to the lag in heat transfer and not to the slowness of the adsorption process itself. The latter, as indicated by pressure measurements, was practically complete in thirty seconds.

heats over the whole mass of the catalyst, then the measured initial heats are not entirely due to adsorption on the most active spots and are therefore lower than would be true if the adsorption process were uniform. The time-temperature curves indicate that the adsorption is uniform for the later portions of carbon monoxide added, *i. e.*, in the region 1.2 to 2.5 cc. adsorbed. In these later stages, therefore, the measured heats are not influenced by effect (b).

Results

Altogether twelve series of measurements of differential heats of adsorption were made. These measurements extended over a period of four months, and during this time the copper retained an almost constant degree of activity as was shown by the fact that, for all the series, the isotherms were reproducible within 10% of the total gas volume adsorbed.

TABLE I
SERIES XI

	Volume of gas Admitted, cc.	Volume of gas Adsorbed, cc.	Resid. press., mm. $\times 10^3$	Galv. def., mm.	Diff. heat of Adsorp., Cal./mol.	Total vol. ads., cc.
1	0.069	0.069	0	5.8	20.3	0.069
2	.113	.113	0	9.3	19.8	.182
3	.082	.082	0	6.4	18.8	.264
4	.121	.121	0	Not measured		.385
5	.082	.082	0	6.2	18.2	.467
6	.133	.133	0	9.7	17.5	.600
7	.108	.108	2	7.5	16.7	.708
8	.077	.076	4	5.2	16.5	.784
9	.093	.092	5	6.4	16.5	.876
10	.092	.091	6	5.8	15.5	.967
11	.144	.143	10	9.1	15.3	1.110
12	.164	.161	19	10.1	15.1	1.271
13	.241	.235	34	14.6	14.9	1.506
14	.295	.279	77	16.8	14.5	1.785
15	.194	.176	128	10.5	14.2	1.961
16	.407	.337	320	19.0	13.5	2.298
Total	2.415	2.298				

The data for four typical series are shown in Fig. 3; and for one series in Table I. In these, and in all the other measurements not shown, there is a marked decrease in the heat effect with increasing concentration of gas on the surface. For reasons already given, the values reported for the stages from 1.2 to 2.5 cc. adsorbed represent the true differential heats. But for the stages 0 to 1.2 cc. adsorbed, the values reported are probably lower than the true differential heats. Certainly, we believe, they are not higher.

Because there was no reason to suspect defects in the earlier work for the later stages of ad-

sorption, and because the method in use was not well adapted for high residual gas pressures, the measurements were not extended beyond the 2.5 cc. adsorbed stage corresponding to 0.3 mm. pressure.⁷

Discussion

Two papers have dealt with the differential heats of adsorption of carbon monoxide on copper over the pressure range of 0 to 100 mm. Both investigations were carried out in vacuum jacketed glass calorimeters, but with different thermometers. Beebe³ used a Beckmann thermometer, and Taylor and Kistiakowsky,⁸ a platinum resistance thermometer. The values found by the two methods for the later portions (beyond 1 mm. pressure) were in good agreement, indicating that the heats remained almost constant with a tendency toward a slow decrease in value with increasing concentration of gas on the surface. But in the early stages (0 to 1 mm. pressure) the results were in serious disagreement. Beebe found that the initial value was 30.0 Calories per mole and that the differential heats fell off sharply to about 10.0 Calories per mole at 1 mm. pressure. Taylor and Kistiakowsky, on the other hand, found a very complex relationship between the differential heats and the concentration of gas on the surface in the low pressure stages.

In the opinion of the authors, the calorimetric methods used in both the above researches were unreliable in the stages of residual pressure 0 to 1 mm., owing to the subsequently discovered defects due to slow heat transfer and non-uniform adsorption, sources of error not taken care of in the design of the calorimeters. It should be noted, however, that the previous work of Beebe reporting high initial heats is substantiated in a qualitative sense in the work reported in this paper.

Attention must be called to the work of Ward^{4a}

(7) Because of the nature of the isotherm at 0°, if the volume adsorbed at 100 mm. residual pressure be taken as unity, approximately one-third of that volume is adsorbed at 0.5 mm. and two-thirds at 3 mm. The stages of adsorption will therefore be designated in terms of the residual pressures.

(8) Taylor and Kistiakowsky, *Z. physik. Chem.*, **75**, 341 (1927).

and Beebe,³ both of whom found practically constant heats for hydrogen on copper. As has already been mentioned, the measurements by Beebe for hydrogen and the measurements here reported for carbon monoxide were made on the same copper. The authors offer no theoretical explanation for this apparent difference in the behavior of the two gases. Because of improvements in the technique for measurements at ice-water temperature, the time-temperature curves found in the present work were much smoother than those found by Beebe for hydrogen adsorption. Unfortunately the calorimeter described in this paper is not suitable for measuring differential heats for hydrogen adsorption because this gas is much less strongly adsorbed than is carbon monoxide and because the residual gas pressure is much greater. Using another type of calorimeter and the improved technique, the differential heats for hydrogen will be studied further.

Two of the adsorption reactions which have been most carefully studied with the purpose of detecting and eliminating possible sources of error in the measurements of differential heats, are the reaction of oxygen with charcoal and of carbon monoxide with copper. In both, the differential heats decrease in a marked degree with increasing concentration of gas on the adsorbent surface. Pending further experimental work, it will be necessary to account for these data on some basis other than that of faulty method.

Summary

1. In a calorimeter designed to eliminate as far as possible all the known sources of error, the differential heats of adsorption have been measured for carbon monoxide on copper at 0°.
2. In the initial stages, the differential heats decrease in a marked degree as successive small portions of the gas are added to the surface.
3. Qualitatively, this work substantiates previous work by Beebe.

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