

oxygen double bond distance is about 1.21 Å. instead of 1.24 Å. The structure of acetaldehyde is discussed briefly in terms of resonance among several valence-bond structures.

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RECEIVED AUGUST 10, 1939

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

## The Heat of Combustion of *cis*- and *trans*-Azobenzene<sup>1</sup>

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In making theoretical calculations of bond energies, Pauling<sup>2</sup> called attention to the unsatisfactory character of the data on the heat of combustion of azobenzene, and a redetermination of this quantity was undertaken in this Laboratory. While the investigation was still in the early stages, Hartley<sup>3a</sup> reported the preparation of the compound in the two isomeric forms, *cis*- and *trans*-, theoretically to be expected but previously never isolated. The two forms exist in equilibrium in solution, transition to the *cis* form being favored by sunlight. In the solid form the *cis* isomer is reported to be stable. In all previous work with azobenzene, therefore, the possibility exists that undetermined percentages of the two forms may have been present.

With this knowledge at hand the standard methods of purification were modified to take advantage of Hartley's findings in order that the two separate isomers might be prepared in the pure state, and the heat of combustion determined for each. In addition these results permit a new approach to the determination of the heat of transition, which has been measured by Hartley<sup>3b</sup> by another method.

**The Calorimeter.**—The calorimeter system and its calibration have been described previously in detail.<sup>4</sup> The heat of combustion of the *trans* isomer was measured before certain structural changes had been made in the system and hence the energy equivalent was somewhat different from that described in the reference cited. At the time of the work on *trans*-azobenzene the energy equivalent of the calorimeter (without the charge) was found to be 2507.6, 2507.5, 2506.9

(2505.4), 2507.9, 2507.1, with a mean value of  $2507.4 \pm 0.4$  cal. deg.<sup>-1</sup>. For the combustion of *cis*-azobenzene the calorimeter equivalent was that for which details are given,<sup>4</sup>  $2550.0 \pm 0.2$  cal. deg.<sup>-1</sup>.

The results of this paper are given in conventional calories calculated from international joules by dividing by the factor 4.1833<sup>5</sup> and are referred to the standard temperature of 25° in the same manner as previously.<sup>4</sup>

**Preparation of Compounds.**—Hartley<sup>3</sup> has shown that the formation of the *cis* form is favored by solar radiation, and that, being more polar, this form is consequently more soluble in polar solvents, this preferential solubility being the basis of the separation of the two forms.

Various samples of azobenzene were therefore recrystallized from aqueous ethanol and methanol, and from benzene and chloroform, all in very dim light. All the samples melted at 68.0–68.1° (by the capillary tube method) against a thermometer calibrated by the Bureau of Standards, and were combined for a final recrystallization from aqueous acetone. Any possible small amount of the *cis* form present originally should have been converted due to the temperature effect, or left in solution, it being thirty times as soluble in water as the *trans*-azobenzene. The product was dried in the dark over phosphorus pentoxide and melted at 68.1°. The minimum time for drying of these samples before combustion was eight days.

For the preparation of *cis*-azobenzene the most recent method of Hartley was used.<sup>3b</sup> A saturated solution of azobenzene in glacial acetic acid (500 cc.) was insolated for several hours in bright sunlight, keeping it in an ice-bath to reduce the temperature. This precaution was found to be imperative though not mentioned by Hartley. From this point all operations were carried out in the darkroom. Four hundred fifty cc. of water was added to precipitate the major portion of the *trans*-azobenzene and the solution filtered. The filtrate was diluted further with 500 cc. of water and extracted with chloroform. The extract was washed with water and evaporated immediately with reduced pressure. The products from several exposures were united and recrystallized twice more from petroleum ether (b. p. 40–60°) at temperatures from 20 to –10°, each time being washed with liberal portions of the solvent. The melting point of the compound measured by the "dip" method used by Hartley was 71.6°, slightly above the m. p. (71.4°), previously reported for the substance. The

(1) Taken from a thesis submitted by R. J. Corruccini toward the M. A. degree, Oregon State College, July, 1939. Published with the approval of the Monographs Publication Committee, Oregon State College, as Research Paper No. 26, School of Science, Department of Chemistry.

(2) Pauling, *THIS JOURNAL*, **54**, 3570 (1932).

(3) (a) Hartley, *Nature*, **140**, 281 (1937); (b) *J. Chem. Soc.*, 633 (1938).

(4) Hughes, Corruccini and Gilbert, *THIS JOURNAL*, **61**, 2639 (1939).

(5) Rossini, *Chem. Rev.*, **18**, 233 (1936).

compound was kept in the dark over phosphorus pentoxide for four days with no observable change in the m. p., and seven determinations of the heat of combustion were then made. One was discarded because of carbon formation.

The remainder of the compound was then again recrystallized from petroleum ether, no change being observed in the m. p. It also was dried for four days over phosphorus pentoxide in a refrigerator and two more combustions made.

Checking against possible loss due to volatility, a standard sized sample was found to lose only *ca.* 0.02 mg. in weight per hour, which is therefore negligible, since the combustion always followed weighing within less than this interval of time.

### Results

The results for the combustion of *trans*-azobenzene are given in Table I, and for *cis*-azobenzene in Table II. The "precision error" of the determinations has been calculated by the method

TABLE I

THE ISOTHERMAL HEAT OF COMBUSTION OF *trans*-AZOBENZENE AT 25°

Energy equivalent of the calorimeter 2507.4 ± 0.4 cal. deg.<sup>-1</sup>

True mass of sample, g.	Corr. <sup>a</sup> temp. rise, deg.	Total heat evolved, cal.	Cal. from HNO <sub>3</sub>	-ΔU <sub>B</sub> /m, cal. g. <sup>-1</sup>	Dev. from mean
0.68454	2.3171	5818.8	11.4	8483.6	+0.3
.73356	2.4840	6238.0	14.0	8484.7	+1.4
.73534	2.4881	6248.5	13.1	(8479.6)	(-3.7) <sup>b</sup>
.73119	2.4750	6215.4	12.9	8482.8	-0.5
.73868	2.5003	6279.0	12.5	8483.4	+ .1
.73187	2.4770	6220.5	13.1	8481.5	-1.8
.72606	2.4578	6172.2	12.5	8483.7	+0.4
			Mean =	8483.3	±0.8

<sup>a</sup> Corrected for heat of stirring, evaporation, etc., and for the energy of ignition of the iron wire. <sup>b</sup> Not used in obtaining the mean.

TABLE II

THE ISOTHERMAL HEAT OF COMBUSTION OF *cis*-AZOBENZENE AT 25°

Energy equivalent of the calorimeter 2550.0 ± 0.2 cal. deg.<sup>-1</sup>

True mass of sample, g.	Corr. <sup>a</sup> temp. rise, deg.	Total heat evolved, cal.	Cal. from HNO <sub>3</sub>	-ΔU <sub>B</sub> /m, cal. g. <sup>-1</sup>	Dev. from mean
0.70053	2.3460	5991.3	11.9	8535.6	-1.8
.70482	2.3606	6028.7	11.6	8537.2	-0.2
.70636	2.3680	6047.6	13.1	(8543.0)	(+5.6) <sup>b</sup>
.73077	2.4477	6251.2	12.4	8537.3	-0.1
.74352	2.4909	6361.6	12.3	8539.5	+2.1
.72306	2.4222	6186.0	12.0	8538.8	+1.4
.72857 <sup>c</sup>	2.4407	6233.4	12.5	8538.4	+1.0
.71989 <sup>c</sup>	2.4105	6156.3	11.9	8535.2	-2.2
			Mean =	8537.4	±1.2

<sup>a</sup> Corrected for heat of stirring, evaporation, etc., and for the energy of ignition of the iron wire. <sup>b</sup> Not used in obtaining the mean. <sup>c</sup> These samples were recrystallized once more than the first six samples.

of Rossini.<sup>5</sup> For the *trans* form the accuracy uncertainty assigned to the heat of combustion of the standard benzoic acid (39 e) by the Bureau of Standards is 0.023%. The calibration error "c" of the first calorimeter was 0.015% and the reaction error "b" for the combustion of *trans*-azobenzene was 0.01%. The resulting accuracy error was 0.03%.

Similarly for the *cis*-azobenzene, the calibration error "c" was 0.006% and the reaction error "b" 0.014%. Including with these a reasonable allowance of 0.03% for possible lack of purity of the *cis* form, the accuracy uncertainty for this isomer becomes ±0.04%. The question of the purity is obviously an important one. The only criterion available to us was the m. p., which is obviously not of the same order of accuracy as the heat measurements. However, the fact that repeated crystallization failed to change either the m. p. or the heat of combustion gives reasonable confidence in the purity of the compound. Swietoslowski and Bobinska report<sup>7</sup> that their azobenzene was prepared by vacuum distillation and melted at 68.35–68.40°. Samples prepared in our laboratory by this method (three distillations *in vacuo*) melted at 68.1°, the temperature which we obtained for pure *trans*-azobenzene prepared by crystallization. As a further check, all of the *cis* residues which had been through several additional steps of treatment in their preparation were reconverted to the *trans* by heating to 135° for fifteen minutes, at which temperature the *cis*-*trans* transition is instantaneous.<sup>8b</sup> The *trans*-azobenzene thus formed likewise showed the original melting point of 68.1°.

From -ΔU<sub>B</sub>, the heat evolved in the bomb process per gram formula weight, -ΔU<sub>R</sub>, the decrease in energy for the combustion reaction at the standard state as defined by Washburn<sup>6</sup> was calculated. In doing this it was assumed that the nitrogen produced in the combustion may be treated as if it were oxygen. -ΔH<sub>R</sub>, the heat evolved in the isothermal process in the standard state at constant pressure was also calculated. These results for *trans*-azobenzene are shown in Table III where are also collected the results of other investigators. It seems apparent that in the most recent work, that of Swietoslowski and Bobinska,<sup>7</sup> the azobenzene must have been essentially the pure *trans* form. Since this work

(6) Washburn, *Bur. Standards J. Research*, **10**, 544 (1933).

(7) Swietoslowski and Bobinska, *Roczniki Chem.*, **9**, 723 (1929).

was done before the Washburn corrections were available, and with different conversion units, etc., quantitative comparison is difficult. The value reported by Swietoslowski to the Bureau of Standards is different from that in his published work.

TABLE III  
COMPARISON OF DATA ON *trans*-AZOBENZENE

Investigator	$-\Delta U_B$	$-\Delta H_B^a$ kcal. mole <sup>-1</sup>	$-\Delta H_R$
Petit <sup>a</sup>		1555.2	
Lemoult <sup>b</sup>		1552.6	
S. and B. <sup>c</sup>	1543.7	1544.6	
S. <sup>d</sup>		1545.9	
This paper	1545.7	1546.6	1545.6

<sup>a</sup> Petit, *Ann. chim. phys.*, [6] 18, 145 (1889). <sup>b</sup> Lemoult, *ibid.*, [8] 13, 562 (1908). <sup>c</sup> Swietoslowski and Bobinska, ref. 7. <sup>d</sup> Swietoslowski, private communication to U. S. Bur. Stds.; see Kharasch, *Bur. Standards J. Research*, 2, 425 (1929). <sup>e</sup> Heat evolved at constant pressure without Washburn correction to standard reference state.

The comparative results for the two pure forms from the present work are shown in Table IV. From them may be obtained  $-\Delta H$  for the transition *cis*  $\rightarrow$  *trans* at 25°. This amounts to 9.9 kcal. mole<sup>-1</sup> or 54  $\pm$  4 cal. g.<sup>-1</sup>. Hartley<sup>3b</sup> has found by another method 65  $\pm$  4 cal. as the

mean of three determinations. Finally, also,  $-\Delta H_{298.16}^\circ$ , the heat of formation of the compound, may be calculated using 68,318.1 cal. mole<sup>-1</sup> as  $-\Delta H_{298.16}^\circ$  for water and 94,030 cal. mole<sup>-1</sup> for carbon dioxide.<sup>8</sup> These results are shown in Table IV.

TABLE IV  
SUMMARY OF DERIVED DATA ON *cis*- AND *trans*-AZOBENZENE AT 25°

Substance	<i>trans</i> -Azobenzene	<i>cis</i> -Azobenzene
Mol. wt.	182.21	182.21
$-\Delta U_B$ kcal. mole <sup>-1</sup>	1545.7 $\pm$ 0.3 <sup>a</sup>	1555.6 $\pm$ 0.2 <sup>a</sup>
$-\Delta U_R$	1544.7 $\pm$ .4 <sup>b</sup>	1554.6 $\pm$ .6 <sup>b</sup>
$-\Delta H_R$	1545.6 $\pm$ .4 <sup>b</sup>	1555.5 $\pm$ .6 <sup>b</sup>
$-\Delta H_{298.16}^\circ$	-75.65	-85.55

<sup>a</sup> Precision uncertainty. <sup>b</sup> Accuracy uncertainty.

### Summary

1. The isothermal heat of combustion of *cis*- and of *trans*-azobenzene has been determined for 25° and constant pressure.
2. The heat of formation for each has been calculated.
3. The heat of the transition *cis*  $\rightarrow$  *trans* has been calculated.

(8) Rossini, *Bur. Standards J. Research*, 22, 407 (1939).

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RECEIVED JULY 31, 1939

[A CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

## Fluorination of Phosphorus Trichloride<sup>1</sup>

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This investigation is a continuation of the studies by this Laboratory on the fluorination of non-polar inorganic halides.<sup>3-8</sup> Booth and Swinehart<sup>3</sup> reported the action of antimony trifluoride in the presence of a catalyst on phosphorus trichloride to give a smooth evolution of gases of unknown composition. The only chlorofluoride of phosphorus reported in the literature is PF<sub>3</sub>Cl<sub>2</sub> prepared by Moissan.<sup>9</sup>

The generator used in the preliminary study was similar to that shown in Fig. 1A except that the generator head

was attached directly to the flask, without a fractionating column. About 200 g. of reagent grade phosphorus trichloride was placed in the flask, the catalyst was added and powdered sublimed antimony fluoride was fed in, as needed for a smooth reaction, by means of the screw solid feed C, at room temperature. (Approximately two cubic centimeters of the catalyst, SbCl<sub>5</sub>, per 100 g. of PCl<sub>3</sub> was found to be an optimum amount.) With tap water in the generator head, (H), (+15°) the product was largely PF<sub>3</sub>, a small amount of PF<sub>2</sub>Cl and very little or no PFCl<sub>2</sub>.

On the assumption that the fluorination of phosphorus trichloride is stepwise, the application of precise control to the operating variables ought to lead to improvements in the yields of chlorofluorides. In a stepwise reaction probability of excessive fluorination should be a minimum when the reaction zone (generator flask A, Fig. 1A), is maintained at such a temperature that the unfluorinated liquid will be gently boiling and refluxing at the pressure maintained in the system, since then a fluorinated product would immediately distil out of the reaction zone as soon as it was formed, due to its lower boiling point.

The apparatus shown as Fig. 1A was constructed so as to attain this end. The reaction flask A was a two-liter,

(1) Original manuscript received August 24, 1938.

(2) From a thesis presented by A. R. Bozarth, May, 1935, to the Graduate School of Western Reserve University in partial fulfillment of the requirements of the degree of Doctor of Philosophy in Chemistry.

(3) Booth and Swinehart, *THIS JOURNAL*, 54, 4750, 4751 (1932).

(4) Booth and Bozarth, *ibid.*, 55, 3890 (1933).

(5) Booth and Stillwell, *ibid.*, 56, 1531 (1934).

(6) Booth and Swinehart, *ibid.*, 57, 1333 (1935).

(7) Booth and Herrmann, *ibid.*, 58, 63 (1936).

(8) Booth and Morris, *ibid.*, 58, 90 (1936).

(9) H. M. Moissan, "Le Fluor et Ses Composés," 1900, p. 167.