

AN ABSTRACT OF THE THESIS OF

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Although it had been known for some time that there existed the possibility of there being cis and trans isomers of azobenzene, an actual separation of the two forms was not accomplished until 1937. It was found that the two forms possessed slightly different physical properties. Since all previous determinations of the heat of combustion of azobenzene had been made with the ordinary or trans-isomer, it was decided to determine the heats of combustion of the two forms separately. This was done with the adiabatic combustion calorimeter in use in the laboratory of Physical Chemistry.

With the trans-isomer, six determinations gave an average value of 8483.3 cal. gm.⁻¹ for the heat of the bomb process with an average deviation from the mean of + 0.8. Similarly for the cis-form, seven runs gave an average of 8535.7 cal. gm.⁻¹ with an average deviation of + 1.2. The energy equivalent of the calorimeter was determined before each series of experiments by burning samples of standard benzoic acid with a known heat of combustion.

Correction of the data for the bomb process to standard conditions and constant pressure gives values for the heats of combustion of 1543.8 and 1553.4 kcal. mol.⁻¹ for trans and cis-azobenzene, respectively. The former of these values compares well with the most recent of the existing determinations of the heat of combustion of ordinary azobenzene. The uncertainty in these figures has been calculated to be $\pm 0.03\%$ for the trans and $\pm 0.04\%$ for the cis.

THE HEATS OF COMBUSTION OF
TRANS AND CIS-AZOBENZENE

by

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THE HEATS OF COMBUSTION OF TRANS AND CIS-AZOBENZENE

INTRODUCTION

For some time it has been realized that the structural configuration of the azobenzene molecule implies the existence of cis-and trans isomers. Not until the last two years, however, has a successful separation been made of these two forms. Hartley in England has reported (1) that azobenzene as ordinarily prepared consists almost entirely of the trans-isomer, which is the more stable of the two forms. He prepared cis-azobenzene by means of a photochemical conversion of ordinary azobenzene and has studied the kinetics of reactions involving some of its derivatives. The two forms differ in melting point by 3.4°C and differ somewhat in solubilities. The more polar cis-isomer is the more soluble of the two in polar solvents as might be expected. The cis-form has a dipole moment of 3.0 Debye units while the symmetrical trans -isomer has a moment of zero. The cis-form has a greater absorbing power for blue light than the trans, and this fact was made use of by Hartley in a photometric method for determining the concentration of a mixture of the two forms in solution. Unfortunately,

we were not able in this investigation to utilize this method of analysis.

A number of determinations of the heat of combustion of azobenzene have been reported in the literature (5) but no attempt has been made as yet to determine the two isomeric forms separately. Accordingly, it was decided to attempt this with the adiabatic calorimeter in use in this laboratory. Details of the operation of this apparatus are available elsewhere (2) and will not be described here except as they were modified for this particular investigation. The trans-isomer was determined first and the cis some three months later. In the interim, changes were made in the calorimeter system which necessitated a redetermination of its heat capacity. Details of both calibrations of the calorimeter are included here.

THE FIRST CALIBRATION OF THE CALORIMETER

For this calibration fifteen runs were made with standard benzoic acid (Bureau of Standards sample #39e). Full details of the calculation of the energy equivalent of the empty bomb and calorimeter can be found elsewhere (3). For the conditions which obtained during these runs it was possible, by making the required substitutions, to simplify the classical equations of Washburn (7) to the following simple working relations.

$$S_F = 3.51 + 0.542 m - 34 n_{\text{HNO}_3}$$

$$\text{and } S_B = \frac{6315.1 m + 13,960 n_{\text{HNO}_3}}{\Delta T} - S_F$$

Here, S_F is the heat capacity of the contents of the bomb after the combustion in cal. deg.⁻¹, S_B is the heat capacity of the empty calorimeter system in cal. deg.⁻¹, m is the true mass of the sample burned, n_{HNO_3} is the number of mols of nitric acid formed during the combustion (determined by titration of the bomb water after each run) and ΔT is the temperature rise in degrees. It may be calculated (8) that 6315.1 calories are evolved per gram of benzoic acid burned under the conditions existing in our apparatus. 13,960 calories are evolved per mol of nitric acid formed from nitrogen, oxygen, and water at constant volume. Heat of solution of the nitric acid may be neglected.

For our platinum resistance thermometer it was found that $\Delta T = \Delta R / 0.10036$, where ΔR is the change in resistance of the thermometer during a combustion in ohms.

ΔR was corrected for heat of stirring and for the heat given off by the burning of the iron fuse wire by a fixed quantity (0.00118 ohms for twenty minutes stirring and 2.5 cms. of fuse wire). The unit of energy used throughout this paper is the defined conventional calorie which is derived from the international joule by multiplying by the factor $1.0004/4.1850$.

The data obtained is summarized in Table I. All runs were started at 25°C. Runs #1,2,3,4,11,14,15 were discarded because of incomplete combustion resulting in carbon deposits. Runs #6 and 8 were discarded because of gross errors committed during the combustion.

TABLE I

DETERMINATION OF THE ENERGY EQUIVALENT
OF THE CALORIMETER AT 25.0°

Run	True mass benzoic acid, gm.	Temp. rise corr. for stirring and Fe	cal. from benzoic acid	cal. from HNO ₃	Energy equiv. cal. deg. ⁻¹	dev. from mean
5	0.96233	2.4367	6077.2	11.9	2507.6	+0.2
7	0.98191	2.4714	6200.2	5.6	2507.5	+0.3
9*	0.99850	2.5140	6305.6	3.0	(2505.4)	(-2.0)
10	0.98898	2.4892	6245.5	4.4	2506.9	-0.5
12	0.98425	2.4769	6215.6	5.7	2507.9	+0.5
13	0.99714	2.5089	6297.0	2.7	2507.1	-0.3
Mean value					2507.4	<u>+0.4</u>

*not used in obtaining mean

THE HEAT OF COMBUSTION OF trans-AZOBENZENE

Several different samples of azobenzene were treated separately by such various procedures as recrystallization from ethanol or methanol by the addition of water, and recrystallization from chloroform or benzene. All melted at about 68.1° , (Hartley reports a m.p. of 68.0°) after repeated treatment and were combined and given a final recrystallization from acetone solution by the addition of water. Since the cis-isomer can be produced only by the action of light, the solution was kept in a dim light. The addition of the water was believed to have extracted any of the cis-form that might have been produced while the azobenzene was in solution, since the cis-form is about thirty times as soluble in water as the trans. After drying over P_2O_5 in the dark the final product melted at $68.1^{\circ} C$.

One change in operating technique was made in this series of determinations which is worthy of note. Following the calibration of the calorimeter system, experiment had shown that the heat of stirring for a given interval of time was not truly constant. Accordingly, the governed induction-type motor then in use for stirring was replaced by a synchronous motor, since the variation was thought to be due to a variation in the rate of stir-

ring. Further tests showed, however, that the heat of stirring was still not constant but increased slightly during a run. Therefore, the practice was adopted of taking the heat of stirring for a ten-minute period immediately following the initial warm-up period of about twenty minutes. Following this, the ignition of the charge ensued, the calorimeter was run for twenty minutes and the heat of stirring taken for another period of ten minutes. The two values for the heat of stirring for ten minutes so obtained were then added together to give a total which was assumed to be equal to the heat of stirring during the twenty-minute period immediately following the ignition. Experiments showed this procedure to be accurate within the limits of error with which the temperature was determined and its use has been adopted in all subsequent work.

Eighteen combustion runs were made with trans-azobenzene. On a number of these runs nitric acid was tested for in the bomb gases by slowly bubbling them through a spiral tower containing a dilute solution of potassium hydroxide. No nitric acid was ever found within the limits of error of the method of detection.

If the Washburn equations are slightly modified to take into account the presence of nitrogen in the material burned, the heat of the bomb process in calories per gram

is easily calculated (4). Simplification of these relations gives the following working equations, wherein the nomenclature is the same as before.

$$S_F = 3.53 + 0.563 m - 34 n_{\text{HNO}_3}, \text{ cal.deg.}^{-1}$$

$$\text{and } -\Delta U_B/M = (2507.4 + S_F)\Delta T - 13,960 n_{\text{HNO}_3}, \text{ cal.gm.}^{-1}$$

Here $-\Delta U_B/M$ is the heat of the bomb process (e.g. at an initial oxygen pressure of 30 atm., at 25.0°, at constant volume, etc.) in calories per gram.

The results are tabulated in Table II. Runs #2,3,4, 5,6,7,8,11 were discarded because of carbon deposits in the crucible or on the interior of the bomb. Run # 1 gave a low result, apparently because of insufficient drying (40 hours) and was discarded. On runs #13 and 14 the sample was inadvertently allowed to stand for several hours after weighing before being burned. A subsequent experiment showed the loss in weight of a sample over such a period of time to be easily sufficient to account for the low results obtained on these two runs, which were then discarded.

TABLE II

THE ISOTHERMAL HEAT OF COMBUSTION OF
trans-AZOBENZENE AT 25.0°

Run	True mass of sample, gm.	Temp. Rise corr. for stirring and Fe	Total heat evolved cal.	Cal from HNO ₃	$\Delta U_B/M$, cal.gm. ⁻¹	dev. from mean
9	0.68454	2.3171	5818.8	11.4	8483.6	+0.3
10	0.73356	2.4840	6238.0	14.0	8484.7	+1.4
12*	0.73534	2.4881	6248.5	13.1	(8479.6)	(-3.7)
15	0.73119	2.4750	6215.4	12.9	8482.8	-0.5
16	0.73868	2.5003	6279.0	12.5	8483.4	+0.1
17	0.73187	2.4770	6220.5	13.1	8481.5	-1.8
18	0.72606	2.4578	6172.2	12.5	8483.7	+0.4
Mean					8483.3	+0.8

*not used in obtaining mean

THE SECOND CALIBRATION OF THE CALORIMETER

In order to **minimize** such errors as might be caused by variation in the heat of stirring it was decided to decrease the size of the stirring propellers, thus cutting down the absolute magnitude of the correction for this quantity to about one-fifth of its former value (the new heat of stirring is now about 0.0001° rise in temperature per minute). The rate of stirring was not altered. In order to maintain efficient circulation with the smaller blades a partition was placed in the inner can of the calorimeter in such a way as to form a tube surrounding the propellers. This change in turn necessitated a redetermination of the energy equivalent of the calorimeter system. This was made as before except for the change which was described earlier in the manner of determination of the correction for the heat of stirring. A new bottle of standard benzoic acid (Bureau of Standards sample #39e) was used, and several samples were fused before use in order to test the dryness of the material. Fifteen runs were made. The results are summarized in Table III.

A low crucible was used at first, resulting in a number of runs in which carbon was blown out of the crucible onto the walls of the bomb. Substitution of a high-walled crucible partially remedied this difficulty. Runs #1,2,3,

6,7,9,11 were discarded because of the production of carbon.

TABLE III

DETERMINATION OF THE ENERGY EQUIVALENT
OF THE CALORIMETER AT 25.0°

Run	True mass benzoic acid, gm.	Temp. rise corr. for stirring and Fe	cal. from benzoic acid	cal. from HNO ₃	Energy equiv. cal. deg. ⁻¹	dev. from mean
4	0.98753	2.4435	6236.3	2.1	2549.1	-0.4
5	0.99162	2.4535	6262.2	1.7	2549.1	-0.4
8	0.99252	2.4554	6267.9	0.9	2549.1	-0.4
10	0.98488	2.4362	6219.9	1.5	2549.6	+0.1
12*	0.75136	1.8604	4744.9	3.6	2548.6	-0.9
13*	0.62341	1.5420	3937.1	1.5	2550.4	+0.9
14*	0.62438	1.5443	3943.2	0.9	2550.0	+0.5
15*	1.08859	2.6920	6874.8	1.3	2550.1	+0.6
				Mean	2549.5	<u>+0.5</u>

*fused sample

THE HEAT OF COMBUSTION OF *cis*-AZOBENZENE

The method of Hartley (1) was followed in the preparation of the *cis*-isomer of azobenzene. A saturated solution (ca. 8%) of ordinary azobenzene in 500 cc. of glacial acetic acid is placed in a large white dish with a glass cover in bright sunlight. (It was found necessary in our experiments to keep the mixture on a cold bath in order to get a measurable yield.) After about four hours the proportion of *cis*-azobenzene in the mixture becomes steady at about 24%. 450 cc. of water is then added in the dark (this amount has been found to be just enough to precipitate nearly all of the *trans*-isomer but none of the *cis*) and the solution filtered. (The residue may then be used over again.) The solution is next diluted further with 500 cc. of water and extracted with chloroform. The extract is washed with water and evaporated in a vacuum at once, the main essential for a good yield being to get the *cis*-form in the solid state as quickly as possible.

The crude products of several exposures which had been obtained in this way were united and recrystallized twice from petroleum ether (b.p. 40-60°) between room temperature and the temperature of an ice-salt freezing mixture. Each batch of crystals was washed with cold solvent to

remove mother liquor which reportedly may contain a little of the trans-isomer which has been formed by thermal conversion of the cis-form. The melting point of the product was slightly above the 71.4° which Hartley reports as being the melting point of cis-azobenzene. The product was kept in the dark over P_2O_5 for four days before any determinations were made. Then seven runs were made, of which number 6 had to be discarded because of carbon.

Following this the remainder of the sample was recrystallized once more in the same way as before. After being kept in a refrigerator for four days over P_2O_5 , runs 8 and 9 were made. The results are shown in Table IV. The agreement obtained apparently proves conclusively that the sample was pure. Its melting point remained 71.4° after the further recrystallization. A standard size sample was found to lose about 0.02 mg. in weight per hour. This is an entirely negligible rate of loss since each ignition took place within an hour after the weighing of the sample.

TABLE IV

THE ISOTHERMAL HEAT OF COMBUSTION
OF *cis*-AZOBENZENE AT 25.0°

Run	True mass of sample, gm.	Temp. rise corr. for stirring and Fe	Total heat evolved cal.	Cal. from HNO ₃	$-\Delta U_B/M,$ cal.gm. ⁻¹	dev. from mean
1	0.70053	2.3460	5990.1	11.9	8533.9	-1.8
2	0.70482	2.3606	6027.5	11.6	8535.5	-0.2
3*	0.70636	2.3680	6046.4	13.1	(8541.3)	(+5.6)
4	0.73077	2.4477	6250.0	12.4	8535.6	-0.1
5	0.74352	2.4909	6360.4	12.3	8537.8	+2.1
7	0.72306	2.4222	6184.8	12.0	8537.1	+1.4
8	0.72857	2.4407	6232.2	12.5	8536.7	+1.0
9	0.71989	2.4105	6155.1	11.9	8533.5	-2.2
Mean					8535.7	<u>+1.2</u>

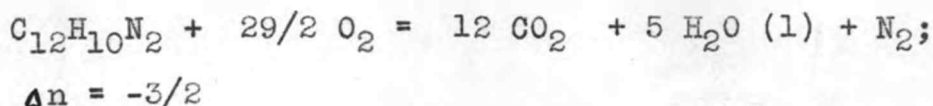
*not used in obtaining mean

DISCUSSION OF THE RESULTS

The results of this investigation which were given in Tables II and IV in terms of calories per gram may now be converted to a molal basis, taking the molecular weight of azobenzene as 182.21. This gives an average value for $-\Delta U_B$, the heat of the bomb process, of 1545.7 kcal.mol⁻¹ for trans-azobenzene and of 1555.3 kcal. mol⁻¹ for cis-azobenzene.

It now becomes necessary to correct these figures to standard conditions in order to obtain $-\Delta U_R$, the change in intrinsic energy of the reaction under standard conditions. (ΔU here corresponds to ΔE in the nomenclature of Lewis and Randall.) This is done very simply by means of the approximate equation given by Washburn (9) assuming that the nitrogen produced by the combustion may be treated as though it were oxygen. A correction of -0.065% ensues as a result of this calculation, and we find that $-\Delta U_R$ is 1544.7 kcal. mol⁻¹ for trans-azobenzene and 1554.3 kcal. mol⁻¹ for cis-azobenzene.

Finally, a simple calculation from the relation, $\Delta H = \Delta U + \Delta nRT$, gives us for $-\Delta H_R$, the heat of combustion at 25.0° and standard conditions, the values of 1543.8 and 1553.4 kcal. mol⁻¹ for trans and cis-azobenzene, respectively, for the pure reaction,



It is now possible to make an interesting comparison with some earlier values for the heat of combustion of ordinary or trans-azobenzene. Kharasch (5) in his review of thermochemical data quotes three values. Of these, a value of 1555.2 kcal.₁₅mol⁻¹ obtained by Petit in 1889 and another of 1552.6 obtained by Lemoult in 1908, may be disregarded in view of the low precision prevailing in the thermochemical work of that time. Kharasch attaches the greatest weight to a value of 1545.9 kcal. mol⁻¹ reported to him in a private communication by Swietoslawski. No mention is made of a reduction having been made of this value to standard conditions, and since this investigation antedated the pioneering work of Washburn by four years, we may assume that no such correction was made. In a subsequent publication, however, (10) Swietoslawski himself reports a value of 8477.0 cal₁₅ gm.⁻¹ in vacuo which (using the new atomic weight of carbon) reduces to a value of 1544.6 kcal.₁₅mol⁻¹ for $-\Delta H_B$ and 1545.5 for $-\Delta U_B$. Here, $-\Delta H_B$ is the heat of combustion at constant pressure without correction to standard conditions. Without a knowledge of the conditions under which Swietoslawski made these determinations, a further

reduction of his data to a common basis with our own becomes impossible. The foregoing discussion is summarized in Table V.

TABLE V
COMPARISON OF THE DATA ON trans-AZOBENZENE

Investigator	$-\Delta U_B$	$-\Delta H_B$ kcal.s. mol ⁻¹	$-\Delta U_R$	$-\Delta H_R$
Petit		1555.2		
Lemoult		1552.6		
Swietoslawski	1545.5	1544.6		
This research	1545.7	(1544.8)	1544.7	1543.8

The "precision error" of our determinations has been calculated according to the method of Rossini (6). An accuracy uncertainty of 0.023% has been assigned to the determination of the heat of combustion of the benzoic acid used to standardize the calorimeter. The calibration error for the first calibration has been calculated to be 0.015% and the reaction error of the determination of the heat of combustion of trans-azobenzene was 0.01%. This gives a precision error for the latter of $\pm 0.03\%$.

Similarly, the calibration error for the second calibration of the calorimeter was 0.017% and the reaction error for the cis-azobenzene was 0.014% giving a precision error for the latter of $\pm 0.03\%$ also.

It is also desirable to assign an "accuracy error" or estimated uncertainty to the final values. In the case of the trans-azobenzene no sources of error other than those involved in the actual determination are known to us and accordingly the accuracy error is equal to the precision error. For the cis-azobenzene, however, we believe that there is a possibility of some slight impurity in the material. Assigning a value of 0.025% to this possible error, we arrive at an accuracy uncertainty for cis-azobenzene of $\pm 0.04\%$. Assignment of a possible 10% error to the Washburn correction does not materially affect the above figures. The data obtained is now summarized in Table VI.

TABLE VI
SUMMARY OF DERIVED DATA AT 25.0°

Substance	trans-azobenzene	cis-azobenzene
Formula	$C_{12}H_{10}N_2$	$C_{12}H_{10}N_2$
Mol. wt.	182.21	182.21
$-\Delta U_B$, kcal. mol ⁻¹	1545.7 ± 0.4 ^a	1555.3 ± 0.5 ^a
$-\Delta U_R$, kcal. mol ⁻¹	1544.7 ± 0.4 ^b	1554.3 ± 0.6 ^b
$-\Delta H_R$, kcal. mol ⁻¹	1543.8 ± 0.4 ^b	1553.4 ± 0.6 ^b

a precision uncertainty
b accuracy uncertainty

This data makes possible one final comparison.

Hartley (1) by indirect measurement found the heat of the transition, cis \rightarrow trans, to be 65 calories per gram and obtained a maximum error of 4 calories in three determinations. Taking the difference between our values of $-\Delta H_R$ for trans and cis-azobenzene we obtain for the same quantity a value of 54 calories per gram with an estimated uncertainty of about ± 4 calories. Without more detailed information as to the possible sources of error in Hartley's measurements we cannot hazard a guess as to the reasons for this discrepancy.

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