dimethylglyoxime noted by Johnson and Hall was also found with this new series of nickel complexes. A 1% ethanolic solution of dimethylglyoxime was added to a methyl cellosolve solution of the complex. All of the complexes which gave an immediate precipitate with dimethylglyoxime also showed rapid nickel exchange. Of those which did not give an immediate precipitate with dimethylglyoxime, only 3 and 17 showed exchange under any of the conditions used. Number 3 gave a precipitate with dimethylglyoxime on standing overnight. It was found to undergo rapid exchange. No. 17 was tested in both methylcellosolve and acetone solution. The methyl cellosolve solution gave no visible precipitate after one hour. However, on standing overnight, a dense precipitate formed. In the acetone solution, a precipitate was barely visible after an hour. After 80 minutes, the precipitate was clearly visible. This slow formation of a precipitate with dimethylglyoxime is interesting in view of the slow exchange this complex was found to undergo.

Comparison with Copper Complexes

Several investigators[14-17] have reported that for certain chelating groups, the copper complexes are more stable than those of nickel (however, see *C. A.*, **44**, 10567*c* (1950)). It is of interest then to compare the exchange behavior of these nickel complexes with that observed for the corresponding copper complexes by Duffield and Calvin.[17] These results are not strictly comparable because of the different solvents used, and it is conceivable that the amount of pyridine present may have a large effect. Nevertheless, the comparison is interesting. It is made in Table II.

TABLE II

EXCHANGE BEHAVIOR OF NICKEL AND COPPER COMPLEXES

	Chelating group	Exchange results Copper complex	Nickel complex
1	Salicylaldehyde	Rapid exchange	Rapid exchange
2	N-Methylsalicylaldimine	Rapid exchange	Rapid exchange
3	Salicylaldehyde-ethylenediimine	Exchanges with a half-time of 2.1 hours	No exchange after 48 hours
4	Salicylaldehyde-*o*-phenylenediimine	Very slow exchange (if any)	No exchange after 48 hours
5	Acetylacetone-ethylenediimine	Exchanges with a half-time of 37 hours	No exchange after 48 hours

This comparison seems to indicate that in cases 3, 4 and 5 above, these complexes are more inert toward exchange than are the corresponding copper complexes.

Acknowledgment.—The financial assistance of the National Research Council, which provided a fellowship for the year 1949–1950, and of the Research Committee of the Graduate School of the University of Wisconsin, which supported this research with funds supplied by the Wisconsin Alumni Research Foundation, is gratefully acknowledged. We are deeply indebted to the microanalytical group of this Laboratory for their assistance.

MADISON 6, WISCONSIN RECEIVED MARCH 14, 1951

---

(14) P. Pfeiffer, H. Thielert and H. Glaser, *J. prakt. Chem.*, *N. F.*, **152**, 145 (1939).

(15) D. P. Mellor and L. Maley, *Nature*, **161**, 436 (1948).

(16) M. Calvin and N. C. Melchior, THIS JOURNAL, **70**, 3270 (1948).

(17) R. B. Duffield and M. Calvin, *ibid.*, **68**, 557 (1946).

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

The Heats of Combustion of Some Nitrogen Compounds and the Apparent Energy of the N–N Bond[1a,b]

BY LELAND G. COLE[2a,b] AND E. C. GILBERT

The N–N and N=N bond energy terms in some substituted hydrazines and in azobenzene have been evaluated from new isothermal heats of combustion of *p*-nitroaniline, 4,4′-dinitrohydrazobenzene and hydrazobenzene. A lower mean N–H bond energy term derived from recent data on hydrazine was used in the computations and compared with similar results using the adjusted N–H bond energy term for ammonia. The N–N energy terms resulting from use of the proposed lower N–H term are self-consistent and in agreement with chemical experience. The N=N bond energy term agrees with that obtained recently for the resonance-free azoisopropane molecule. Certain assumptions involved in the reduction of experimental data obtained in this Laboratory and the experimental technique on nitrogen-containing substances were tested by redetermination of the heat of combustion of hippuric acid; the value so obtained is shown to agree with the precise value of Huffman when his value is adjusted for a subsequent change in the benzoic acid standard.

Introduction

The chemical bond energy terms[3] may be obtained for the bonds A–X and A–Y of a molecule of general type AX_aY_b with little certainty in as much as the intramolecular influences of A–Y on an assigned mean value for the energy of the A–X bond previously determined from the type molecule AX_c are not known or quantitatively predictable. Further, it is known that the A–X bonds may have c energies for the formation,

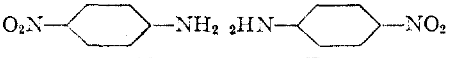
---

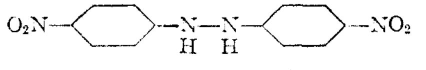
(1) (a) Published with the approval of the Monographs Publication Committee, Oregon State College as Research Paper No. 184, School of Science, Department of Chemistry. (b) For material supplementary to this article order Document 3334 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

(2) (a) Based on theses submitted by Leland G. Cole in partial fulfillment of the requirements for the M.A. and Ph.D. degrees at Oregon State College. (b) Present address: Jet Propulsion Laboratory, California Institute of Technology, Pasadena.

(3) E. T. Butler and M. Polanyi, *Trans. Faraday Soc.*, **39**, 19 (1943); G. E. Coates and L. E. Sutton, *ibid.*, **43**, 1188 (1947). Also see A. D. Walsh, *ibid.*, **43**, 60 (1947) and L. H. Long and R. G. W. Norrish, *Proc. Roy. Soc.* (*London*), **187A**, 337 (1946), for a discussion of the use of the terms dissociation energy, bond energy and bond heat of formation; recently M. Szwarc and M. G. Evans, *J. Chem. Phys.*, **18**, 618 (1950), have analyzed the concepts of bonding energies and discussed this general problem in detail.

respectively, of AX_{c-1}, AX_{c-2}, etc., from AX_c after the removal of one atom of X, two atoms of X, etc., each energy of which would, of course, produce a different value for the A–Y energy term. For complex molecules such as the substituted hydrazines the assignment of bond energies by a mean energy method is, at best, only qualitatively useful. However, Anderson and Gilbert[4] have used an approach in which errors in bond energy assignments, resonance energy differences, etc., are reduced to a minimum by comparison of the heats of combustion of structurally similar molecules. The argument can be shown most efficiently by the graphical comparisons, for example, of two moles of *p*-nitroaniline and 4,4′-dinitrohydrazobenzene


(1)


(2)

It is obvious that the energy of formation of two moles of *p*-nitroaniline (1) in the gaseous state differs from that of a mole of gaseous 4,4′-dinitrohydrazobenzene (2) chiefly by the energy of two N–H bonds and the energy of the N–N bond. Estimations for the N–N bond energies in a series of hydrazines or hydrazobenzenes and for the N–N bond energies in azobenzenes therefore depend on the assigned energy value for the N–H bond.[4–7]

Certain assumptions involved in the computations of the isothermal heats of combustion of nitrogen-containing compounds are tested and our technique checked by redeterminations on hippuric acid; our value agrees with that reported by Huffman[8] when his value is adjusted for the change in the presently accepted values for the standard samples of benzoic acid.[9]

Experimental

The Calorimeter.—The adiabatic calorimeter used in the present investigation has been described previously.[4,6] The apparatus was recalibrated with National Bureau of Standards Benzoic Acid, Sample No. 39f, and found to have an energy equivalent of 2608.36 defined calories per degree (±0.62 mean deviation from the mean). After determining the heats of combustion of *p*-nitroaniline, 4,4′-dinitrohydrazobenzene and some nitrostilbenes,[10] a minor alteration of the 34-junction thermocouple was made and a recalibration revealed no change in heat capacity of the system. After determining the heat of combustion, with the thermocouple so altered, of hydrazobenzene, a new 34-junction thermocouple was constructed and installed; a recalibration revealed a change in calorimeter energy equivalent to 2609.15 defined calories per degree (±0.64 mean deviation from the mean). Determinations of the heat of combustion of hippuric acid were made subsequent to this recalibration.

The precision attainable under optimum conditions with this calorimeter is 0.01 to 0.02%.

Materials. Benzoic Acid.—National Bureau of Standards Sample No. 39f was used for which freezing point determinations and titrations had indicated purities of 99.98 and 100.03 mole per cent. benzoic acid. When burned under standard conditions and referred to 25°, the heat of combustion of this sample is now taken to be 26,428.4 int. joules $g.^{-1}$ (*in vacuo*).[9] This value was adjusted by −1.0 int. joule $g.^{-1}$ for changes from standard procedure in the masses of acid formed and water used in the bomb. An indicator was used throughout, for the determination of the residual nitric acid, which was not affected by carbon dioxide. The presently accepted value of the heat of formation of nitric acid has been used with appropriate modifications of the Washburn equations. The earlier results from this Laboratory[4,6,10,11] may be revised by increasing by 0.039% the energy equivalents of the calorimeter. (Data pertinent to the discussion of the present paper are thus shown correctly in Table II.) The nitric acid correction is within the standard mean deviation and may be neglected.

***p*-Nitroaniline.**—*p*-Nitroaniline was recrystallized from acetone and dried at 85° for 24 hours and over phosphorus pentoxide at room temperature for two days. The sample melted at 146.5–147.0° and pellets therefrom showed no trend in heat of combustion after varying lengths of time.

4,4′-Dinitrohydrazobenzene.—This substituted hydrazobenzene was prepared according to the method of Green and Bearder[12] by oxidation of *p*-nitroaniline with calcium hypochlorite and reduction of the resulting 4,4′-dinitroazobenzene with colorless ammonium sulfide. The product was recrystallized from boiling acetone containing small amounts of alcohol, dried at 140° for 24 hours and over phosphorus pentoxide for two days in a vacuum desiccator twice rinsed with dried nitrogen gas.

Hydrazobenzene.—Hydrazobenzene was prepared by the reduction of azobenzene with zinc dust and sodium hydroxide in an inert atmosphere. After a 72-hour drying period in a dry-nitrogen rinsed desiccator over phosphorus pentoxide, a melting point in air of 128.5–129.0° was recorded. Further drying of a portion of the sample for 200 hours failed to produce a measurable change in the melting point and no definite trend in the heat of combustion was observed.

Hippuric acid.—Eastman Kodak (White Label) hippuric acid was recrystallized three times from distilled water and dried at 105° for 48 hours and over phosphorus pentoxide for from 72 to 96 hours.

Calculations.—All weights are *in vacuo*. The data are referred to a standard temperature of 25°. The energy unit used is the arbitrary calorie which is defined as equal to 4.1833 international joules.

The heat evolved at the experimental conditions per gram formula weight, $-\Delta U_B$, was calculated first from observations of the resistance change of the thermometric bridge, determinations of the heat evolved from the nitric acid formed, and the true mass of sample in grams. $-\Delta U_R$, the decrease in energy for the combustion process at the standard state at constant volume was then calculated by the method of Washburn.[13] In making this calculation the nitrogen was treated as oxygen and the correction equations modified appropriately. $-\Delta H_R$, the heat evolved in the isothermal process in the standard state at constant pressure and $-\Delta H_f$, the standard heat of formation from the elements were calculated from the experimental results using the atomic weights of 1949 and the most recent values[14] for the heats of formation of carbon dioxide and liquid water.

Results.—The experimental results of the combustion determinations are summarized in Table I for hydrazobenzene, 4,4′-dinitrohydrazobenzene, *p*-nitroaniline and hippuric acid. The isothermal heats of combustion and of formation are summarized in Table II with earlier results from this Laboratory revised for changes in the accepted value for the benzoic acid standard and for changes in the heats of formation of carbon dioxide and water. The value of $-\Delta U_B/m$ for methylhydrazine is that reported by Aston.[15]

---

[4] C. M. Anderson and E. C. Gilbert, THIS JOURNAL, **64**, 2369 (1942).

[5] L. Pauling, "The Nature of the Chemical Bond," Second Edition, Cornell University Press, Ithaca, N. Y., 1945, p. 55.

[6] A. M. Hughes, R. J. Corruccini and E. C. Gilbert, THIS JOURNAL, **61**, 2639 (1939).

[7] K. S. Pitzer, *ibid.*, **70**, 2140 (1948).

[8] H. M. Huffman, *ibid.*, **60**, 1171 (1938).

[9] R. S. Jessup, *J. Research Natl. Bur. Standards*, **29**, 247 (1942).

[10] C. M. Anderson, L. G. Cole and E. C. Gilbert, THIS JOURNAL, **72**, 1263 (1950).

[11] (a) R. J. Corruccini and E. C. Gilbert, *ibid.*, **61**, 2925 (1939); (b) G. F. Davies and E. C. Gilbert, *ibid.*, **63**, 1585 (1941); (c) E. C. Gilbert and G. F. Davies, *ibid.*, **63**, 2730 (1941).

[12] A. G. Green and E. A. Bearder, *J. Chem. Soc.*, **99**, 1966 (1911).

[13] E. W. Washburn, *J. Research Natl. Bur. Standards*, **10**, 525 (1933).

[14] D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer and F. D. Rossini, *ibid.*, **34**, 143 (1945).

[15] J. G. Aston, *et al.*, private communication, October 28, 1949, *cf.* Reports #5 and #6 of Task Order III, Contract N6 ONR-269, Cryogenic Laboratory, Chemistry Department, Pennsylvania State College (November 1, 1948 and April 1, 1949).

TABLE I

HEATS OF COMBUSTION

Substance	Calorimeter constant (defined cal. deg.$^{-1}$)	$-\Delta U_B/m$ (cal./g.)	Standard deviation (cal./g.)
Hydrazobenzene	2608.36	8636.9	±2.72
4,4-Dinitrohydrazobenzene	2608.36	5464.7	±1.86
p-Nitroaniline	2608.36	5504.2	±0.04
Hippuric acid	2609.15	5631.6	±2.29

The experimental molar heats of combustion of the present paper are compared with previously reported values in Table III. The heat of combustion of 4,4'-dinitrohydrazobenzene had not been reported previously. The average deviations of the experimental heats of combustion are 0.024% for hydrazobenzene, 0.030% for the dinitrohydrazobenzene, 0.002% for *p*-nitroaniline and 0.037% for hippuric acid. The heat from HNO_3 formed during combustion varies from 0.2 to 0.3% of the total heat. Swietoslawski and Bobinska[16] have reported a heat of combustion at 20° of 8617.4 ± 4.3 cal. g.$^{-1}$ for hydrazobenzene (15° calories, sample weighed *in vacuo*) as compared with the present value of 8636.9 ± 2.0 cal. g.$^{-1}$. Previous experience has indicated that their results may be on the low side.[11a] Swietoslawski and Bobinska reported a slightly lower melting point for hydrazobenzene than observed here. Pongratz, *et al.*,[17] report an "unpublished" result of W. A. Roth of 8632.7 ± 1.6 g.$^{-1}$, presumably at conditions similar to ours.

TABLE II

ISOTHERMAL HEATS OF COMBUSTION AND FORMATION AT 25.0°

Substance	$-\Delta U_B/m$ (cal./g.)	$-\Delta U_R$ (kcal./mole)	$-\Delta H_R$ (kcal./mole)	$-\Delta H_f$ (kcal./mole)	Ref.
Aniline	8703.5	810.05	810.79	− 7.37	4
cis-Azobenzene	8540.7	1555.9	1556.8	− 86.59	11b
trans-Azobenzene	8486.6	1545.8	1546.7	− 76.49	11b
Benzamide	7010.1	848.56	849.00	48.47	4
Dibenzoylhydrazine	6976.0	1674.8	1675.4	51.23	4
4,4'-Dinitrohydrazobenzene	5464.7	1497.3	1496.4	− 26.20	This work
Diphenylamine	9053.3	1531.0	1532.3	− 27.93	4
Hydrazine	4639.4	148.68	148.68	− 12.05	6
Hydrazobenzene	8636.9	1590.2	1591.4	− 52.9	This work
Methylhydrazine	6764.9	311.64	311.94	− 12.94	15
p-Nitroaniline	5504.2	759.64	759.34	9.92	This work
Phenylhydrazine	8058.5	870.97	871.57	− 33.99	4
Tetraphenylhydrazine	9063.5	3047.2	3049.6	−109.2	4

TABLE III

MOLAR HEATS OF COMBUSTION AT 25.0°

(Constant pressure)

Substance	$-\Delta H_R$ (kcal./mole) This paper	Literature	Observer
p-Nitroaniline	759.34	761.5	Roth and Macheleldt[a]
		760.2	Swarts[b]
		771.4	Kharasch[28]
4,4'-Dinitrohydrazobenzene	1496.4	....	....
Hydrazobenzene	1591.4	1587.8	Swietoslawski and Bobinska[16]
		1590.3	Roth (reported by Pongratz, *et al.*[17])
		1605.5	Lemoult[31]
		1600.2	Petit[c]
Hippuric acid	1008.3	1008.2	Huffman[8]

[a] W. A. Roth, R. Macheleldt, Dissertation, Braunschweig, 1921. [b] Work of Swarts, reported by W. E. Garner and C. L. Abernathy, *Proc. Roy. Soc.* (*London*), **99**, 213 (1920). [c] M. P. Petit, *Ann. chim. phys.*, [6] **18**, 145 (1899).

The heat of combustion of hippuric acid agreed very satisfactorily with the value reported by Huffman.[8] This agreement with Huffman's proposed secondary standard validates with reasonable certainty our experimental technique and the methods of computation employing the Washburn equations modified to account for the presence of large amounts of nitrogen among the reaction products.

Discussion

The Energy of the N-N Bond.—The N–N bond energy terms in the series of hydrazines were evaluated from a mean-valued term for the N–H bond in ammonia after Pauling.[4] However, use was made of Gaydon's more recent and substantially higher dissociation energy for nitrogen[18] in evaluating the heat of atomization of ammonia; hence, the higher N–H bond energy term (93.4 kcal. at 25°). Since resonating structures of the type $\overset{-}{N}(\overset{+}{H})_3$ present in ammonia are not possible in hydrazine, Skinner[19] has proposed the use of a slightly lower N–H bond term of 92.0 kcal., or 1.4 kcal., less than the mean; this value was subsequently adopted by Pitzer.[7] The N–N bond energy terms were also evaluated for an assumed lower N–H bond energy term of 88.0 kcal. derived from a consideration of the following facts. Szwarc[20] has determined the activation energy for dissociation of the N–N bond in hydrazine and the heat of dissociation of the first N–H bond in ammonia to be 60 ± 3 kcal., and 104 ± 2 kcal., respectively, while that of the third N–H bond, *i.e.*, in the NH radical, has been determined by Glockler[21] to be 85 kcal. From a consideration of the N–H bond lengths in NH_3 (1.014 Å.) where the first N–H bond energy is 104 kcal., and in the NH radical (1.038 Å.), where the N–H bond energy is 85 kcal., the N–H bond energy in hydrazine may be expected to be near that of the N–H radical since the N–H bond length in hydrazine is 1.04 ± 0.06 Å.[22] Further support for the use of a lower N–H bond energy term in the hydrazines appears on evaluation of the N–H bond in hydrazine itself using Szwarc's recent N–N dissociation energy of 60.0 ± 3.0 kcal. From the

---

[16] W. Swietoslawski and J. Bobinska, *Roczniki Chem.*, **9**, 723 (1939).

[17] A. Pongratz, S. Böhmert-Süss and K. Scholtis, *Ber.*, **77B**, 651 (1944).

[18] A. G. Gaydon, *Nature*, **153**, 407 (1944).

[19] H. A. Skinner, *Trans. Faraday Soc.*, **41**, 652 (1945).

[20] M. Szwarc, *Proc. Roy. Soc.* (*London*), **A198**, 267 (1949).

[21] G. Glockler, *J. Chem. Phys.*, **16**, 602 (1948).

[22] P. A. Giguère and V. Schomaker, THIS JOURNAL, **65**, 2025 (1943).

heat of atomization of hydrazine and this N-N bond value, a mean N-H bond energy term of 88.0 kcal. is obtained which is nearer the NH radical value than the first N-H bond energy in NH_3 by 6.5 kcal. as qualitatively expected from the previous consideration of bond lengths. The N-N bond energy terms obtained using the N-H term values of 93.4 and 88.0 kcal. are summarized in Table IV.

TABLE IV

N-N BOND ENERGY TERMS FROM HEATS OF COMBUSTION

Compounds compared	Bond energy (kcal.) (N-H) = 93.4 State Standard	Gaseous	(N-H) = 88.0 State Standard	Gaseous
Hydrazine	48.7	38.5	70.2	60.0
Methylhydrazine	50.2[a]	41.0[a]	55.6[a]	46.3[a]
Methylamine and ammonia	54.9[b]	45.3[b]	60.3[b]	50.6[b]
Phenylhydrazine	45.1	42.5	50.4	47.8
Aniline and ammonia				
Tetraphenylhydrazine	29.3	41.3[c]	18.5	30.5[c]
Diphenylamine				
Dibenzoylhydrazine	36.9	46.9[c]	26.2	36.2[c]
Benzamide				
Hydrazobenzene	44.5	48.5[c]	33.7	37.7[c]
Aniline				
4,4'-Dinitrohydrazobenzene	36.6	53.8[c]	25.8	43.0[c]
p-Nitroaniline				
Methylphenylhydrazine	41.1	33.1[c]	46.4	38.4[c]
Methylaniline and ammonia				

[a] Calculated from data of Thomsen.[27] [b] Calculated from data of Muller.[26] [c] Heats of sublimation known or estimated as follows: diphenylamine, 21 kcal. mole^{-1}; tetraphenylhydrazine, 30 kcal. mole^{-1}; benzamide, 20 kcal. mole^{-1}; dibenzoylhydrazine, 30 kcal. mole^{-1}; hydrazobenzene, 20 kcal. mole^{-1}; *p*-nitroaniline, 23.6 kcal. mole^{-1}; 4,4'-dinitrohydrazobenzene, 30 kcal. mole^{-1}. Heat of fusion, aniline, 1.9 kcal. mole^{-1}.

Use of the N-H bond energy term of 88.0 kcal. results in a N-N bond term in gaseous tetraphenylhydrazine of 30.5 kcal. It is interesting to note the agreement of this value with that of Cain and Wiselogle[23] who have determined an activation energy of dissociation for this bond of 30.0 ± 1.5 kcal. This close agreement would be meaningful if the activation energy for association of diphenyl nitrogen radicals was very low. Lewis,[24] in fact, has estimated this activation energy of association to be <1 kcal.

The N-N bond energy terms in phenylhydrazine and hydrazobenzene, for the N-H term assumption of 88.0 kcal., were calculated from the present data to be 47.8 and 37.7 kcal., respectively; these values are in good agreement with the experimentally determined activation energies of dissociation of Dewar, as reported by Szwarc,[25] of 48 kcal., per mole of phenylhydrazine and of 35-36 kcal., per mole of hydrazobenzene, making the reasonable assumption again that the activation energies for association are very small. The bond energy terms from the present work are compared with the available dissociation energy data in Table V.

TABLE V

ENERGIES OF SOME N-N BONDS (KCAL.)

Substances	Bond energy terms from heats of combustion	Heats of dissociation (experimental)
Hydrazine	60.0	60.0 ± 3
Phenylhydrazine	47.8	48
Hydrazobenzene	37.7	35-36
Tetraphenylhydrazine	30.5	30.0 ± 1.5

The N-N bond energy terms in methylhydrazine derived from Aston's combustion data for methylhydrazine[15] and from Muller and Thomsen's data[26,27] for methylamine, as revised by Kharasch,[28] are lower than in hydrazine, apparently as a result of partial withdrawal of the lone pair of electrons on nitrogen into the methyl group by resonance. The higher apparent energy for the N-N bond in 4,4'-dinitrohydrazobenzene than in hydrazobenzene for both assumed values of the N-H bond energy term is in agreement with the observations of Wieland[29] who found that one *p*-nitro group noticeably reduced the dissociation of substituted hydrazines while two *p*-nitro groups reduced the dissociation still more. The partial withdrawal of the lone pairs on the nitrogens into the ortho and para positions in the phenyl groups results in reduced coulombic repulsion of the nitrogens and, hence, an increased N-N bond energy term. These results support the contention of Lewis and Lipkin[24] that the heat of dissociation of the N-N bond in substituted hydrazines may be related directly to the extent of resonance stabilization in the adjoining phenyl groups. In conclusion it is interesting to note that a still higher heat of dissociation of nitrogen of 289.4 kcal., would yield a mean N-H bond energy term in ammonia of 104 kcal. (in agreement with the experimentally determined dissociation energy of the first N-H bond in ammonia[20]); using this N-H term in hydrazine would result in a N-N term of 59.5 kcal., in agreement with the experimentally determined value of 60.0 kcal.[20]

The Energy of the N=N Bond.—Coates and Sutton[30] have obtained bond energy terms for the nitrogen-nitrogen double bond from heats of combustion of the azo-paraffins which are free from extra-resonance energies. For azoisopropane a N=N bond energy term of 100.3 kcal., was obtained for the standard state, using atomization data similar to those in the present paper. By the comparison method used here to evaluate the N-N bond terms, we have obtained a N=N bond term of 103.5 kcal., in *trans*-azobenzene from the heats of formation of one mole of this substance and of two moles of aniline, assuming a N-H bond energy term of 93.4 kcal. Similarly, the *cis*-isomer possesses a N=N bond energy term of 93.4 kcal. For an assumed N-H term of 88.0 kcal., these N=N energies are 82.0 kcal., and 71.9 kcal., respectively, for the *trans*- and *cis*-azobenzenes or 2.43 and 2.13 times the N-N single bond in hydrazobenzene.

---

(23) C. K. Cain and F. Y. Wiselogle, THIS JOURNAL, **62**, 1163 (1940).

(24) G. N. Lewis and D. Lipkin, *ibid.*, **63**, 3233 (1941).

(25) M. Szwarc, *Chem. Revs.*, **47**, 151 (1950); *cf.* M. J. S. Dewar, *Trans. Faraday Soc.*, in press (1951).

(26) J. A. Muller, *Ann. chim. phys.*, [8] **20**, 116 (1910).

(27) J. Thomsen, *Z. physik. Chem.*, **52**, 343 (1905).

(28) M. S. Kharasch, *J. Research Natl. Bur. Standards*, **2**, 359 (1929).

(29) H. Wieland, "Die Hydrazine," Ferdinand Enke, Stuttgart, 1913.

(30) G. E. Coates and L. E. Sutton, *J. Chem. Soc.*, 1187 (1948).

It would be surmised that the comparison method, in giving such good agreement for the N=N bond in the azobenzenes and azoparaffins, has effectively reduced the resonance and other energy differences to a minimum so that bond energies in a series of related compounds may be quantitatively evaluated by this method. However, the lower N=N bond energy terms obtained on comparison of the azobenzenes with hydrazobenzene in the standard state (for *trans*-azobenzene N=N is 59.0 kcal., for a N–H of 93.4 kcal., and 48.3 kcal., for a N–H of 88.0 kcal.; for *cis*-azobenzene N=N is 48.9 kcal., for a N–H of 93.4 kcal., and 38.2 kcal., for a N–H of 88.0 kcal.,) were not to be expected.

Calculation of the N=N bond energy term in *p*-aminoazobenzene from the combustion data of Lemoult,[31] making use of the heats of combustion of *p*-phenylenediamine[32] and of aniline, yields 104 kcal., for a N–H bond energy term of 93.4 kcal., and 82.7 kcal., for an assumed N–H bond energy term of 88.0 kcal., in agreement with that in *trans*-azobenzene calculated here by comparison with two moles of aniline.

[31] M. P. Lemoult, *Ann. chim. phys.*, [8] **14**, 184, 289 (1908).

[32] G. Kibler and H. Hunt, *J. Phys. Colloid Chem.*, **53**, 955 (1949).

PASADENA, CALIF. RECEIVED FEBRUARY 16, 1951

[CONTRIBUTION FROM THE TONAWANDA LABORATORY, LINDE AIR PRODUCTS COMPANY, A DIVISION OF UNION CARBIDE AND CARBON CORPORATION]

Sodium and Potassium Tungsten Bronzes[1,1a]

BY E. O. BRIMM, J. C. BRANTLEY, J. H. LORENZ AND M. H. JELLINEK

A study of the sodium tungsten bronzes, potassium tungsten bronzes and sodium–potassium tungsten bronzes has been made. Methods are presented for preparing a series of sodium–potassium tungsten bronzes of violet color and tetragonal structure. A new sodium–potassium tungsten bronze has also been prepared. It is a dark blue, needle-like crystal; the structure appears to be hexagonal. The solubility of the sodium tungsten bronzes, $NaWO_3$ to $Na_{0.8}WO_3$, in sodium tungstate has been demonstrated. New electrical properties of the tungsten bronzes as electrodes in aqueous solutions are described. They are, in general, excellent conductors of direct current when used as cathodes. As anodes, the blue sodium tungsten bronzes conduct in all electrolytes. All other tungsten bronzes conduct as anodes only in alkaline reducing electrolytes. X-Ray studies and chemical analyses of the tungsten bronzes have been used to study their structure and composition. A new value of 3.8622 Å. is reported for the lattice constant of cubic $NaWO_3$. The tetragonal potassium tungsten bronzes and sodium–potassium tungsten bronzes have lattice constants of about $a = 12.28$ Å. and $c = 3.82$ Å., there being variations from these values for varying compositions. Sodium tungsten bronze has catalytic activity in the decomposition of formic acid but not in the dehydrogenation of *n*-heptane.

Sodium tungsten bronzes were first reported by Wöhler,[2] potassium tungsten bronzes by Laurent.[3] The preparation and properties of the sodium tungsten bronzes have been studied by Hägg,[4] Straumanis[5,6] and Magnéli.[7] The properties of the potassium tungsten bronzes are not well known although several methods for their preparation have been described.[8,9,10] Recently Magnéli[11] has reported the crystal structure of tetragonal potassium tungsten bronze.

In addition to tungsten bronzes containing only sodium or potassium, a mixed sodium–potassium tungsten bronze has been described.[8,12] This bronze is reported to consist of purple-red needles, but no other properties are given. It was prepared by hydrogen or tin reduction of a mixture of sodium and potassium paratungstates.

The work of Straumanis[5,6] and Magnéli[7,11] was published soon after an investigation into the properties of the alkali metal tungsten bronzes had been started in this Laboratory. We report here on certain extensions of their work as well as some new data on the properties of the sodium and potassium tungsten bronzes and the mixed sodium–potassium tungsten bronzes.

Materials.—All of the materials used in the preparation of the tungsten bronzes were of reagent grade. Sodium tungstate dihydrate was dehydrated by heating at 120° for 24 hours. Potassium tungstate was prepared from tungsten (VI) oxide and potassium carbonate by fusing the solids, extracting the tungstate with water and recrystallizing the potassium tungstate. It was then dried at 120° for 24 hours.

Analytical Procedures.—The tungsten bronzes were analyzed by standard procedures. A weighed sample was digested with ammonium sulfate and sulfuric acid. Tungsten was precipitated with cinchonine and determined as tungsten(VI) oxide.[13] No correction was made for silica. The alkali metal content of the filtrates was determined by precipitating the sodium as sodium uranyl zinc acetate and the potassium as potassium perchlorate.[14] The error in these determinations was such that there was an uncertainty of ±0.02 in the value of x in Na_xWO_3.

Sodium Tungsten Bronzes

Preparation of the Sodium Tungsten Bronzes.—Although numerous methods have been proposed for the preparation of sodium tungsten bronzes,[2,10,15] the method of Straumanis[5] was found to produce a wider variety of tungsten bronzes

---

[1] Na_xWO_3 and K_xWO_3 where x varies from 0.15 to 1.0 for the sodium tungsten bronzes and 0.40–0.55 for the potassium bronzes. In addition, $Na_xK_yWO_3$ is known in which the sum of x and y is between 0.20 and 0.55. (a) The material in this paper was originally submitted September 22, 1950.

[2] F. Wöhler, *Pogg. Ann.*, **2**, 350 (1824).

[3] A. Laurent, *Ann. chim. phys.*, **67**, 215 (1838).

[4] G. Hägg, *Z. physik. Chem.*, **B29**, 192 (1935); *Nature*, **135**, 874 (1935).

[5] M. E. Straumanis, THIS JOURNAL, **71**, 679 (1949).

[6] M. E. Straumanis and A. Dravnieks, *ibid.*, **71**, 683 (1949).

[7] A. Magnéli, *Arkiv Kemi*, **1**, 269 (1949).

[8] G. v. Knorre, *J. prakt. Chem.*, **27**, 49 (1883).

[9] E. Zettnow, *Pogg. Ann.*, **130**, 240 (1867).

[10] O. Brunner, Dissertation, Zurich, 1903.

[11] A. Magnéli, *Arkiv Kemi*, **1**, 213 (1949).

[12] W. Feit, *Ber.*, **21**, 134 (1888).

[13] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Company, New York, N. Y., 1946, p. 728–729.

[14] *Ibid.*, p. 414–418.

[15] J. Phillip, *Ber.*, **15**, 506 (1882); V. Spitzin, *Z. anorg. allgem. Chem.*, **148**, 69 (1925); D. van Duyn, *Rec. trav. chim.*, **61**, 669 (1942); L. Kahlenberg and H. H. Kahlenberg, *Trans. Am. Electrochem. Soc.*, **46**, 188 (1924).