193. *Heats of Combustion and Molecular Structure. Part IV.* Aliphatic Nitroalkanes and Nitric Esters.*

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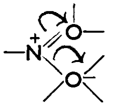
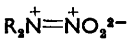
The heats of combustion of nitromethane, nitroethane, 1-nitropropane, 2-nitropropane, dimethylnitramine, and diethylnitramine have been measured. The group-energy terms for the ($C-NO_2$) and ($N-NO_2$) groups are derived from these data and that for ($O-NO_2$) from published data. The significance of the results is considered.

Analysis of the molecular energetics (mean bond- and resonance-energy terms) for the $X-NO_2$ system, where $X = R_3C$, R_2N, and RO, is of general interest and particularly desirable in view of the practical importance of thermal data on such compounds. The analysis is complicated by (i) the simultaneous occurrence of formal charge and resonance effects within the grouping (I), (ii) uncertainties in the values of the mean bond-energy terms for the bonds N–O and N=O, and (iii) the probability, when $X = R_2N$ or RO, of additional mesomerism involving the excited structures (II) and (III). We have therefore approached the analysis in stages, evaluating first, from heats of combustion and latent heats, the " group-energy term " for each of the three types of $X-NO_2$ group, $E(C-NO_2)$, $E(N-NO_2)$, and $E(O-NO_2)$. The group-energy term is the enthalpy change, $-\Delta H$, for the hypothetical gas-phase formation of the nitro-group, *e.g.*, $E(C-NO_2)$ is $-\Delta H$ for $R_3C\cdot + N + 2O \longrightarrow R_3C-NO_2$, *i.e.*, the group energy is that part of the atomic heat of formation, $-\Delta H_{f,a}$, of the nitro-compound corresponding to the actual formation and attachment of the nitro-group, and includes formal charge and resonance effects, mean bond-energy terms, and any additional mesomeric effects. These group-energy terms can be used directly in the evaluation of $-\Delta H_{f,a}$ terms for hypothetical nitro-compounds of all three classes.


(I)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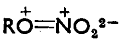
(II)


$R\overset{+}{O}=\overset{+}{N}O_2{}^{2-}$

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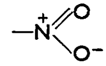
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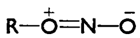
$R-\overset{+}{O}=N-\overset{-}{O}$

(V)

We have attempted to carry the analysis a stage further and to disentangle the various components of the group-energy terms.

Experimental

Materials.—Benzoic acid. The B.D.H. thermochemical standard product ($-\Delta U_b = 6{\cdot}3181 \pm 0{\cdot}0007$ kcal./g.†) was used.

Nitroalkanes. These (I.C.I.) were each distilled through an 18 in. column packed with glass helices. Fractions collected were: nitromethane, b. p. 99·7—99·9°/750 mm. (lit.,[1]

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* Parts I—III, *Trans. Faraday Soc.*, 1954, **50**, 815; *J.*, 1954, 2764; 1955, 1188.

† 1 Thermochemical calorie ≡ 4·1840 abs. Joules.

[1] Heilbron and Bunbury, " Dictionary of Organic Compounds," London, 1946.

100·8°/760 mm.); nitroethane, b. p. 114·0—114·1°/750 mm. (lit.,[1] 114—114·8°/760 mm.); 1-nitropropane, b. p. 128·2—128·4°/732 mm. (lit.,[1] 130·5—131·5°/760 mm.); 2-nitropropane, b. p. 120·0—121·0°/760 mm. (lit.,[1] 120°/760 mm.).

Nitramines. Dimethyl- and diethyl-nitramine were prepared by dehydration of dimethyl- and diethyl-ammonium nitrate, respectively.[2] *NN*-Dimethylacetamide, formed as an impurity in this preparation of diethylnitramine, was removed by 3 hours' refluxing with 85% w/w sulphuric acid.[3] The nitramines were distilled through an 8 in. column packed with Fenske helices. Fractions collected were: dimethylnitramine, b. p. 64·0—64·4°/9 mm. (Chute, Herring, Toombs, and Wright give 70°/25 mm.); diethylnitramine, 53·2°/2 mm. (Backer[4] gives 93°/16 mm. and 206·5°/757 mm.). The dimethylnitramine, five times recrystallised from ether, had m. p. 55·0—55·3° (Chute *et al.*[2] give 57°). Dimethylnitramine was also prepared by the nitrolysis of *as.*-dimethylurea.[5] This specimen, recrystallised five times from light petroleum, had m. p. 55·0—55·2°.

Combustion Calorimetry.—The nitroalkanes were burnt in the stainless steel, single valve, Mahler–Cook bomb of energy equivalent, *E*, 31,199 ± 8·0 cal./ohm, by the procedure described in Part III. Results are shown in Table 1.

TABLE 1.

$m_{(\text{vac})}$ (g.)	ΔR (ohm)	Corrections (cal.) Fuse	HNO_3	Carbon	C (cal./ohm)	$-\Delta U_b$ * (kcal./mole)
		Nitromethane, $M = 61·04$				
2·4646	0·22566	83·7	22·0	0·4	10·1	174·5
1·9613	0·18376	93·1	20·9	0·5	8·0	175·1
1·7572	0·16418	90·6	19·5	0·5	7·2	174·5
		Nitroethane, $M = 75·07$				
1·5337	0·21762	94·1	20·7	2·4	10·3	326·8
1·4283	0·20191	80·6	13·4	0	9·6	326·9
1·3195	0·18743	99·2	17·4	7·1	8·9	326·5
		1-Nitropropane, $M = 89·09$				
1·4531	0·25280	107·8	25·5	1·96	11·1	481·7
0·9880	0·17377	96·4	11·1	2·35	7·6	479·4
1·0032	0·17755	102·5	13·7	1·96	7·6	481·8
1·0160	0·17760	105·4	13·3	1·96	7·8	482·1
1·0630	0·18759	69·2	14·8	0	8·1	483·4
		2-Nitropropane, $M = 89·09$				
1·2529	0·21487	98·5	19·2	0·7	9·6	477·8
1·1645	0·20402	108·6	14·4	0·5	8·9	478·5
0·9318	0·16244	77·1	7·3	2·0	2·0	477·6
0·8627	0·15102	87·9	12·2	3·9	6·6	477·5

* Where $-\Delta U_b = 10^{-3}M/m\,[(E + C)\Delta R -$ corrections for fuse + nitric acid + carbon$]$.

The nitramines were burnt in a twin-valve bomb (the Parr Instrument Company, Moline, Illinois, U.S.A.), made of Carpenter 20 alloy and having an internal volume of 340 ml. The inlet and outlet valves are seated in Kel-F plastic. The sample to be burnt was placed in a flat platinum crucible, supported by a platinum ring attached to the inlet tube. The energy equivalent, *E*, of the calorimeter system containing this Parr bomb was determined, by burning benzoic acid pellets, as 39,980·0 ± 24·0 cal./ohm.

The twin-valve arrangement allows the gaseous products of combustion to be swept out of the bomb and analysed. The amount of carbon dioxide present in the bomb gases after combustion was estimated in an analysis train similar to that described by Prosen and Rossini.[6] The following figures are typical for the quotient of (observed)/(calculated) CO_2 in calibration experiments: 1·0007, 0·9993, 1·0001, 1·0000. When dimethylnitramine was burnt there was produced 99·1—99·6% of the calculated quantity of carbon dioxide. As no carbon was evident and a slight smell of nitramine remained, the heat of combustion was calculated by assuming that the carbon dioxide produced represented the nitramine burnt.

When burning the liquid diethylnitramine, a small amount of petroleum jelly was used with

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[2] Chute, Herring, Toombs, and Wright, *Canad. J. Research*, 1948, **26**, *B*, 95 and 129.

[3] Lamberton, personal communication.

[4] Backer, *Sammlung Chem. Vorträge*, 1912, **18**, 359.

[5] Franchimont, *Rec. Trav. chim.*, 1896, **15**, 211.

[6] Prosen and Rossini, *J. Res. Nat. Bur. Stand.*, 1941, **27**, 289.

the filter paper fuse. The heat of combustion of the petroleum jelly was taken as 11·4 kcal./g. from controls.

Diethylnitramine burnt violently, and in two combustions the Neoprene sealing ring in the head of the bomb was burnt. This was avoided by inserting a platinum crucible about 2 cm. above the sample, as a baffle. Combustion was then incomplete to the extent of about 1%, and carbon was deposited; corrections were made by taking the heat of combustion of carbon as 7·838 kcal./g. Results are given in Table 2.

TABLE 2.

$m_{(vac.)}$ (g.)	$\frac{\text{Obs.}}{\text{Calc.}}CO_2$	ΔR (ohm)	Corrections (cal.)				C (cal./ohm)	$-\Delta U_b$ * (kcal./mole)
			Fuse paper	Fuse jelly	HNO_3	Incomplete combustion		
			Dimethylnitramine, $M = 90\cdot10$					
1·8658	0·9941	0·19459	6·0	—	34·4	45·9	12·6	377·4
1·8109	0·9909	0·18898	6·0	—	33·6	68·8	12·2	376·0
1·7558	0·9948	0·18343	6·0	—	36·4	38·1	11·8	376·1
1·8089	0·9958	0·18928	6·0	—	34·9	31·8	12·2	376·5
			Diethylnitramine, $M = 118\cdot14$					
0·3415	0·9941	0·05116	6·4	38·8	5·3	6·4	1·0	692·3
0·4121	0·9867	0·06118	6·0	25·1	4·3	17·6	1·0	695·6
0·5822	0·9990	0·08091	12·4	35·3	12·2	1·7	1·0	694·1

* Where $-\Delta U_b = 10^{-3}M/m\,[(E + C)\Delta R$ − corrections for fuse paper + fuse jelly + nitric acid − incomplete combustion].

The $-\Delta U_b$ terms were converted into $-\Delta H_c^0$ terms, the standard heat of combustion (Table 3), through the expression

$$-\Delta H_c^0 = -\Delta U_b - w - \Delta n\boldsymbol{R}T$$

where w is the Washburn correction, calculated according to Prosen,[7] and Δn is the number of molecules of gas produced in the combustion of one molecule of the substance.

Independent $-\Delta H_c^0$ data on the nitroalkanes were (*a*) published (Holcomb and Dorsey [8]) during the preliminary stages of our study, and (*b*) made available recently in personal communication from the National Bureau of Standards, Washington. These data are listed for comparison in Table 3. Our $-\Delta H_c^0$ values for the nitroalkanes correspond well with those from both other sources except for nitromethane, where the Bureau value for $-\Delta H_c^0$, 169·5 kcal./mole, is significantly lower than ours and is in accord with the value 169·4 kcal./mole

TABLE 3.

	Nitromethane	Nitroethane	1-Nitropropane	2-Nitropropane	Dimethylnitramine	Diethylnitramine
Mean $-\Delta U_b$ (kcal./mole)	174·4	326·7	481·7	477·8	376·5	692·4
Deviation (%)	0·17	0·10	0·14	0·06—	0·10	0·15
Washburn correction, w (kcal./mole)	0·20	0·22	0·26	0·26	0·08	0·35
$\Delta n\boldsymbol{R}T$ (kcal./mole)	+0·15	−0·15	−0·45	−0·45	+0·30	−0·30
$-\Delta H_c^0$ (kcal./mole):						
This work	174·4 ± 0·3	326·6 ± 0·3	481·8 ± 0·7	478·0 ± 0·3	376·1 ± 1·0	692·4 ± 2·0
Holcomb and Dorsey	175·25 ± 0·18	325·42 ± 0·3	481·22 ± 0·61	477·43 ± 0·17	—	—
N.B.S.	169·49 ± 0·14	324·57 ± 0·25	480·91 ± 0·29	478·17 ± 0·19	—	—
$-\Delta H_f^0$ (kcal./mole)	22·2 ± 0·3	32·3 ± 0·3	39·5 ± 0·7	43·2 ± 0·3	17·0 ± 1·0	25·3 ± 2·0
L_g^{st} (kcal./mole)	9·1 ± 0·1 [a]	9·4 ± 0·1 [a]	10·4 ± 0·1 [a]	9·9 ± 0·1 [a]	16·7 [b]	11·5 *

* Calc. from measurements made by Mr. B. Sutcliffe of the variation of vapour pressure with temperature over the range 65—105°, when $\log_{10} p = 8\cdot302 - 2595/T$, where p is in mm. Hg and T in °K.

[a] Hodge, *Ind. Eng. Chem.*, 1940, **32**, 748. [b] Bradley, Cotson, and Cox, *J.*, 1952, 740.

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[7] Prosen, " Experimental Thermochemistry," ed. Rossini, Interscience, New York, 1956.

[8] Holcomb and Dorsey, *Ind. Eng. Chem.*, 1949, **41**, 2788.

derived by Bichowsky and Rossini[9] from earlier studies. Our $-\Delta H_c^0$ for diethylnitramine is close to the value 69·2 ± 0·9 kcal./mole quoted by Laidler.[10]

Also listed in Table 3 are the terms $-\Delta H_f^0$ (heat of formation of the compound in its standard state from the elements in their standard states, calculated from $-\Delta H_c^0$ by assuming the $-\Delta H_f^0$ terms: H_2O, 68·3174; CO_2, 94·0518 kcal./mole [11]), L_g^{st} (ΔH for the change of the compound in the standard state to the gaseous compound), and the derived $-\Delta H_{f,g}^{st}$ (heat of formation of the gaseous compound from the elements in their standard states).

DISCUSSION

The atomic heats of formation, $-\Delta H_{f,a}$ (Table 4), were calculated from the $-\Delta H_{f,g}^{st}$ terms (Table 3) and the heats of atomisation, ΔH_a, of the elements: C, 171·7;[12] H, 52·09;[11] O, 58·98;[13] N, 113·0[14] kcal./g.-atom.

Group-energy terms are most simply evaluated from $\bar{E}(X\text{–}NO_2) = -\Delta H_{f,a} - \sum'\bar{E}(b)$, in which expression $\sum'\bar{E}(b)$ is the sum of the mean bond-energy terms for all the bonds in the molecule other than those in the X–NO_2 system. However, $\bar{E}$(C–H) is in fact not quite constant among the lower paraffins[15] and use of a constant value for this expression would introduce errors into the evaluation of $\bar{E}(X\text{–}NO_2)$. We therefore evaluate $\bar{E}(X\text{–}NO_2)$ (Table 4) by considering the hypothetical substitution $R_nX\text{–}H + N + 2O \longrightarrow R_nX\text{–}NO_2 + H$, from which $\bar{E}(X\text{–}NO_2) = -\Delta H_{f,a}(R_nX\text{–}NO_2) + \Delta H_{f,a}(R_nX\text{–}H) - \bar{E}(X\text{–}H)$, and use, instead of the general $\bar{E}$(C–H) = 98·85 kcal./mole, the particular values of $\bar{E}$(C–H) derived from the appropriate hydrocarbons by using $\bar{E}$(C–C) = 83·1 kcal./mole,[16] together with those for $\bar{E}$(N–H) and $\bar{E}$(O–H) derived from the appropriate amines and alcohols[16] (Table 4). The $-\Delta H_{f,a}(R_nX\text{–}H)$ terms (Table 4) are derived from the $-\Delta H_{f,g}^{st}$ terms: hydrocarbons:[17] methane, 17·89; ethane, 20·24; propane, 24·82: secondary amines:[18] dimethyl-, 6·6; diethyl-, 20·3: alcohols: methyl,[11] 48·08; ethyl,[11] 56·24; *n*-propyl,[19] 63·64 kcal./mole. The $-\Delta H_{f,a}(RO\text{–}NO_2)$ terms (Table 4) are derived from the corresponding $-\Delta H_{f,g}^{st}$ terms for the nitrate esters:[20] methyl, 29·0; ethyl, 37·0; *n*-propyl, 43·9 kcal./mole.

TABLE 4. $-\Delta H$ *data for* R_nX (*kcal./mole*).

	Me	Et	Pr^n	Pr^i	Me_2N	Et_2N	MeO	EtO	Pr^nO
$-\Delta H_{i,a}$ (R_nX–NO_2)	572·2	857·7	1139·8	1144·0	1000·2	1565·5	646·9	930·8	1213·6
$-\Delta H_{f,a}$ (R_nX–H)	397·9	676·1	956·6	956·6	827·6	1393·1	487·1	771·1	1054·4
$\bar{E}$(X–H)	99·5	99·2	98·7	98·7	93·0	93·0	110·0	110·0	110·0
$\bar{E}(X\text{–}NO_2)$	273·6	280·8	281·9	286·1	265·4	265·4	269·8	269·7	269·2

$\bar{E}(C\text{–}NO_2)$ *Terms from Nitroalkanes.*—The values from nitroethane and the nitropropanes are reasonably concordant, the mean being 282·9 kcal./mole. The value from our (and Holcomb and Dorsey's) nitromethane combustion data, 273·6 kcal./mole, is much lower. $\bar{E}(C\text{–}NO_2)$ derived from the nitromethane data from the National Bureau of

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[9] Bichowsky and Rossini, " The Thermochemistry of the Chemical Substances," Reinhold, New York, 1936.

[10] Laidler, *Canad. J. Chem.*, 1956, **34**, 626.

[11] National Bureau of Standards, Circular 500, Washington, 1952.

[12] Brewer and Kane, *J. Phys. Chem.*, 1955, **59**, 105.

[13] Brix and Herzberg, *J. Chem. Phys.*, 1953, **21**, 2240.

[14] Frost and McDowell, *Proc. Roy. Soc.*, 1956, *A*, **236**, 278.

[15] Prosen and Rossini, *J. Res. Nat. Bur. Stand.*, 1945, **34**, 263.

[16] Coates and Sutton, *J.*, 1948, 1187.

[17] Selected Values of Properties of Hydrocarbons, American Petroleum Institute, Research Project 44, Carnegie Institute of Technology, Pittsburg, 1954.

[18] Thomsen, " Systematische durchsührung Thermochemischer Untersuchungen," Enke, Stuttgart, 1906, p. 343.

[19] Rossini, *J. Res. Nat. Bur. Stand.*, 1934, **13**, 189.

[20] Gray, XXVII Congresso Internacional de Quimica Industrial, 1954.

Standards is 279·4 kcal./mole, much closer to those from the other nitroalkanes. Pending a further study of nitromethane, we take $\bar{E}(C-NO_2) = 283$ kcal./mole for (*a*) computing the $-\Delta H_{f,a}$ terms for hypothetical nitroalkanes, and (*b*) considering the energetics of this grouping.

For the approach to the analysis, to the nearest kcal., of the $\bar{E}(C-NO_2)$ group-energy term, we take $\bar{E}(C-N) = 73$ kcal./mole.[16] This yields 210 kcal./mole for the sum of the bond-energy terms and the formal charge and resonance-energy effects in the group (IV). The resonance energy of the nitro-group is probably *ca.* 25 kcal./mole.[21] A somewhat uncertain value for $\bar{E}(N-O)$, 46 kcal./mole, is available from data on hydroxylamine.[22] Satisfactory data are not available for $\bar{E}(N=O)$, since derivations from results for nitrite esters,[23] R-O-N=O, perforce neglect the effect of resonance with structure (V), etc. The value is likely to be considerably greater than twice $\bar{E}(N-O)$, 92 kcal./mole, since $\bar{E}(N=N)$, 100·3 [16] and $\bar{E}(O=O)$, 118·0 [23] are each greater than twice the corresponding single-bond-energy terms $\bar{E}(N-N)$, 39 and $\bar{E}(O-O)$, 34·9 kcal./mole.[16] We can now estimate the sum of $\bar{E}(N=O)$ and the formal charge effects in the nitro-group as $210 - (25 + 46)$, *i.e.*, 139 kcal./mole.

$\bar{E}(N-NO_2)$ *Terms from Secondary Nitramines.*—The values from dimethyl- and diethyl-nitramines are concordant. We take $\bar{E}(N-NO_2) = 265$ kcal./mole for (*a*) computing $-\Delta H_{f,a}$ terms for hypothetical nitramines and (*b*) considering the energetics of the grouping.

Since the sum of the bond-energy terms and formal charge and resonance-energy effects in the system (IV) is 210 kcal./mole, the contribution of the N-N bonding and the secondary nitramines must be 55 kcal./mole. This is 16 kcal./mole in excess of $\bar{E}(N-N)$, 39 kcal./mole, and implies a considerable contribution to the structure of the isolated molecule from the double bonded N=N structure (II). This structure infringes Pauling's "adjacent-charge rule" [21] but there are already established exceptions to this rule (*e.g.*, in the crystal structure of hydrazinium difluoride [24]). N=N Double-bonding is operative in crystalline dimethylnitramine (Costain and Cox [25]) when the $C_2N_2O_2$ system is coplanar and the N-N distance, 1·26 Å, is much shorter than the normal N-N single-bond distance [26] of 1·40 Å and is close the N=N double-bond distance,[26] 1·20 Å. Confirmation of N=N double bonding in free nitramine molecules also comes from the high dipole moment of dimethylnitramine in benzene, 4·5D.[27]

$\bar{E}(O-NO_2)$ *from Alkyl Nitrates.*—The values are closely concordant and we take $\bar{E}(O-NO_2) = 270$ kcal./mole for (*a*) computing $-\Delta H_{f,a}$ for hypothetical nitrate esters and (*b*) considering the energetics of this grouping.

Since $\bar{E}(-NO_2) = 210$ kcal./mole, the contribution of the O-N bond to $\bar{E}(O-NO_2)$ must be 60 kcal./mole. This is 14 kcal./mole in excess of $\bar{E}(O-N)$, 46 kcal. mole, and implies, analogously to the nitramines, a considerable contribution from the double bonded O=N structure (III), again infringing the adjacent-charge rule. Early electron diffraction studies of gaseous methyl nitrate [28] and an *X*-ray diffraction study of crystalline pentaerythritol tetranitrate [29] did not reveal a shortening of this O-N bond below the single-bond value,[30] 1·37 Å, but it is doubtful if the early techniques were sufficiently

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[21] Pauling, "Nature of the Chemical Bond," Oxford Univ. Press, London, 1950.

[22] Bichowsky and Rossini, "The Thermochemistry of the Chemical Substances," Reinhold, New York, 1936.

[23] Cottrell, "The Strengths of Chemical Bonds," p. 253, Butterworths, London, 1954.

[24] Robertson, *Annual Reports*, 1942, **39**, 102.

[25] Costain and Cox, *Nature*, 1947, **160**, 826.

[26] Sidgwick, "Chemical Elements and their Compounds," Oxford Univ. Press, 1950, p. 709.

[27] Mortimer and Springall, unpublished observations.

[28] Pauling and Brockway, *J. Amer. Chem. Soc.*, 1937, **59**, 13.

[29] Booth and Llewellyn, *J.*, 1947, 837.

[30] Rogowski, *Ber.*, 1942, *B*, **75**, 244.

sensitive (see, *e.g.*, ref. 31) and further diffraction investigation of nitrate esters seems desirable.

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[31] Millar, Mortimer, and Springall, *J.*, 1957, 3456.