Ketelaar (8) reports a value of 214 kcal. per mole. The dissociation energies were obtained from Wilkins (9). Agreement between calculated and measured heat of formation is good.

ACKNOWLEDGMENT

LITERATURE CITED

(1) Adolph, H.G., Osterling, R.E., Taylor, F., Jr., U. S. Naval Ordnance Laboratory, White Oak, Md., private communication.
(2) Baroody, E.E., Wynne, J., Zimmer, M.F., U. S. Naval Propellant Plant NavWeps Report 8686, Tech. Rept. 154, 1964.
(3) Cassel, H.M., U. S. Patent 2,448,768 (Sept. 7, 1948).
(4) Glasgow, P.R., Jr., Streiff, A.T., Rossini, F.D., J. Res. Natl. Bur. Std. 35, 355 (1945).
(5) Good, W.D., Douslin, D.W., McCullough, J.P., J. Phys. Chem. 67, 312-4 (1963).
(6) Good, W.D., Scott, D.W., Waddington, G., Ibid., 68, 1080 (1956)
(7) Jasper, J.J., "Laboratory Methods of Physical Chemistry," pp. 36-9, Riverside Press, Cambridge, Mass., 1947.
(8) Ketelaar, J.A., "Chemical Constitution," p. 191, Elsevier Publishing Co., London, 1953.
(9) Wilkins, R.L., "Theoretical Evaluation of Chemical Propellants," C.N. Bessemer, F.E. Nixon, eds,. Prentice Hall, Englewood, N. J., 1963
(10) Zimmer, M.F., Baroody, E.E., Schwartz, M., McAllister, M.P., J. Chem. Eng. Data 9, 527 (1964).
(11) Zimmer, M.R., Dix, S., Lawrence, A.R., Ibid., 10, 288 (1965).

Heats of Formation and Bond Energies of N-Fluoro-N-nitrobutylamine Isomers

M. F. ZIMMER, E. E. BAROODY, M. G. GRAFF, G. A. CARPENTER, and R. A. ROBB
Research and Development Department, U. S. Naval Propellant Plant, Indian Head, Md.

The heats of formation of the three isomers—normal, secondary, and tertiary—of butyl-N-fluoronitramine are calculated from the heats of combustion as determined with a high precision platinum-lined rotating bomb calorimeter and found to be −38.5 ± 0.4, −37.3 ± 1.0, and −29.9 ± 0.3 kcal. per mole, respectively. The bond energy for N—F in primary $N < ^F_{NO_2}$ is calculated and found to be 67.04 kcal. per mole. The influence of the molecular structure on the heats of formation and bond energies is discussed.

THE INVESTIGATION of the heat of formation and the N—F bond energy was carried out as a part of a program to evaluate N-fluoro-N-nitro compounds.

The reactions of the liquid N-fluoro-N-nitrobutylamines with either diethyloxalate or diethylphthalate as diluents were carried out in an oxygen atmosphere (30 atm.).

The equation of the idealized heat of combustion from which the heat of formation at 298.1° K. and 1 atm. is determined is: $C_4H_9O_2N_2F(l) + 5O_2(g) + 146H_2O(l) \rightarrow 4CO_2(g) + HF \cdot 150H_2O(l) + N_2(g)$. To obtain clean combustion without explosion, the proper ratio of the fluoronitramine compounds to the diluting compounds was determined in a series of preliminary combustions. Best results were obtained with the ratio 35:65 for fluoronitramine to diluting compound.

EXPERIMENTAL

Material. The N-fluoro-N-nitro-n-butylamine (3), and the N-fluoro-N-nitro-(sec- and tert-) butylamine (7) were synthesized and then purified by distillation. The purification of these materials was difficult since all three isomers are unstable at room temperature, with the tert compound being the least stable. Because of this instability and the high volatility of the material, none of the usual chromatographic methods could be applied to check the purity of the material.

The samples were distilled several times in high vacuum at low temperature (0° C.) and checked by IR spectro-

photometer and refractive index measurements. When no changes in the IR curves and refractive indices were detected between subsequent distillations, the samples were used for combustion measurements. Table II lists some properties of the three isomers.

The high instability and volatility of these fluoronitramines made the measurements extremely difficult. Sometimes the material had to be purified between subsequent combustion runs (especially the tertiary compound).

Apparatus. The combustion experiments were carried out in a platinum-lined rotating bomb calorimeter built according to a design of the Bureau of Mines, Bartlesville, Okla. (5). The modifications to the original instrumentation have been described earlier (18).

Procedure. Essentially, the standard procedure was used as reported previously (18). Both the butylfluoronitramine and the diluting agent were sealed in a polypropylene bag, and the bag was placed in the platinum crucible of the bomb. The quantities of the material were chosen to give a temperature rise in the calorimeter of approximately 1.5° C.

Heats of Combustion and Formation. The auxiliary data used in the combustion energy calculations are listed in Table I.

The heats of combustion and formation are summarized in Table II. The average deviation from the mean in these measurements was 0.0%. Data reduction was performed on a digital computer for which a special program had.

	Density, G./Ml.	C_p, Cal./ Deg. G.	$(\partial E \partial P)T$, Cal./Atm.-G.
n-$C_4H_9N_2O_2F$	1.5	0.21[a]	−0.006[a]
sec-$C_4H_9N_2O_2F$	1.1	0.21[a]	−0.006[a]
$tert$-$C_4H_9N_2O_2F$	1.1	0.21[a]	−0.006[a]
Diethylphthalate	1.12(9)	0.40[a]	−0.0063[a]
Diethyloxalate	1.079(9)	0.43[a]	−0.0063[a]
Polypropylene bag	0.9(8)	0.315[a]	−0.0008(16)
Thread	1.5(16)	0.40(15)	−0.007[a]

[a] Estimated.

Table II. Properties of Liquid N-Fluoro-N-nitro-(n-,sec-, and $tert$-) butylamine

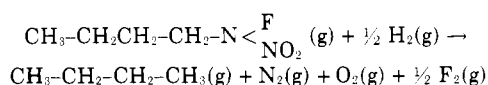|	n-	sec-	$tert$-Butyl-N-fluoronitramine	
Density	1.244	[a]	1.228	20° C. g./ml.
Refractive index	1.4020	1.4007	1.4009	25° C.
Vapor pressure	1.4(2.9° C.)	14(24° C.)	3.3(5.6° C.)	mm. of Hg
	2.9(15.1° C.)		6.9(16° C.)	
	17.(35°)			
H_c	5043.8 ± 2.6[b]	5052.7 ± 7.8[b]	5107.0 ± 6.8[b]	cal./g.
H_f	−38.5 ± 0.4	−37.3 ± 1.0	−29.9 ± 0.3	kcal./mole

[a] This value has not been determined. [b] Average data of six to eight measurements and estimated standard deviation of the mean.

been developed (1). To correct for the heat of solution of CO_2 in $HF \cdot H_2O$, data of Cox and Head (2) were used.

To calculate the heat of formation of the N-fluoronitrobutylamines the following heats of formation at 298° K. were used: $CO_2(g)$, −94,051.8 cal. per mole; $H_2O(l)$, −68,317.5 cal. per mole; and $HF \cdot 150H_2O(l)$, −75,695 cal. per mole.

The heat of vaporization of n-butyl-N-fluoronitramine was estimated from the vapor pressures and found to be 13.0 kcal. per mole. It is assumed that the heats of vaporization of the sec and $tert$ compounds are in the same range. With this estimate, the heat of formation of the gaseous N-fluoro-N-nitro-n-butylamine is −25.5 kcal. per mole.

N—F Bond Energy. To estimate the N—F bond energy in the normal butyl compound, the following hypothetical reaction is considered:

$$CH_3-CH_2CH_2-CH_2-N{<}^{F}_{NO_2} (g) + \tfrac{1}{2} H_2(g) \rightarrow$$
$$CH_3-CH_2-CH_2-CH_3(g) + N_2(g) + O_2(g) + \tfrac{1}{2} F_2(g)$$

Thus,

$$\Delta H_r = \Delta H_f[\text{butane(g)}] - \Delta H_f[R-N{<}^{F}_{NO_2}(g)] =$$
$$E(N—F) + E(C—N) + E(N—N) + E(NO_2) + \tfrac{1}{2} E(H—H) -$$
$$E(N \equiv N) - \tfrac{1}{2} E(F—F) - E(O—O) - E(C—H)$$

For the bond energies, the following values in kcal. per mole have been used:

$E(C—N)(4) = 67.4$; $E(H—H)(4) = 104.18$; $E(N—N)(4) = 60.0$

$E(NO_2) = 212$; $E(N \equiv N)(17) = 225.93$; $E(F—F)(17) = 37.72$

$E(O—O) = 119.1(17)$, $E(C—H)(4) = 99.297$

The bond energies for $-N{<}^{O}_{O}$ were determined from the heats of formations of seven different nitramines and nitro compounds. Ketelaar (11) reports a value of 214 kcal./mole. From these values and the heats of formation for butane (g) (−30.15 kcal. per mole) and N-fluoro-N-nitro-n-butylamine (−25.5 kcal. per mole) the bond energy for N—F is calculated and found to be $E(N—F) = 67.04$ kcal. per mole. Good, Douslin, and McCullough found $E(N—F) = 67$ kcal.

per mole and Marantz (14) $E(N—F) = 68.9$ kcal. per mole.

These results indicate that the N—F, bond is very little influenced by the proximity of the nitro group.

By using the equation

$$\Delta H_{f298} = -\sum_i n_i q_i + \sum_j (\Delta H_A)_j$$

one obtains for the fluoronitro-n-butylamine $\Delta H_{f298} = 38.7$ kcal. per mole (with $E(N—F) = 67.0$ kcal. per mole) (4) or $\Delta H_{f298} = 40.6$ kcal. per mole (with $E(N—F) = -68.9$ kcal. per mole). In Equation 1, n_i and q_i are the number and the bond energy respectively, of the i-th bond in the molecule and $(\Delta H_A)_j$ is the heat of formation of the j-th gaseous atom produced by complete decomposition of the compound.

This method of calculation does not take into account the energy changes caused by the molecular structure.

Branching of a paraffin chain causes a lowering of the heat of formation. Lehmann (13) reports that a change from a n-paraffin chain to a sec-paraffin with the structure —CH— causes a change of −1.50 kcal. per mole in the heat of formation. Klages (12) reports a value of −1.7 kcal. per mole for $tert$-paraffins which has to be added to the calculated heat of formation in order to account for the structure. This correlation does not hold for the isomers of the butylamine, since variation in the observed H_f values are in the opposite direction. Table III lists the heats of formation of some butanes, butyl alcohols, and butylamines.

Considering the experimental heats of formation of the isomeric N-fluoro-N-butylamines (Table II) it is clear that

Table III. Heats of Formation in Kcal./Mole of Butane, Butyl Alcohol, and Butylamine.

	Butanes(10)	Butyl Alcohols(9)	Butylamines(9)
n-	−29.81(g)[a]	−67.81(g)[a]	−41.35
sec-	−31.45(g)	−69.05(g)	−38.95
$tert$-			−36.95

[a] (g) = gas

the change in the heats of formation cannot be accounted for by the values reported in the literature for the molecular configuration of the paraffin chain. This leads to the conclusion that there is an interaction between the iso-alkyl group and the fluoronitramine group. The difference between the heats of formation of the normal and sec-butyl-N-fluoronitramines is in the range of differences reported for many other isomeric compounds (Table III). However, there is a "jump" in the heat of formation from the sec- to the tert-butyl-N-fluoronitramine. The difference between these isomers is unusually high, but is supported by decomposition rate studies. The n- and sec-butyl-N-fluoronitramines show approximately the same decomposition rate $(0.8.10^{-4}$ sec.$^{-1})$; the tertiary compound has a twenty times higher decomposition rate $(24.10^{-4}$ sec$^{-1})$ (6).

It is assumed that branching of the butyl chain introduces strain into the molecule by steric hindrance and electronic configuration.

ACKNOWLEDGMENT

This investigation was supported by the Bureau of Naval Weapons, Department of the Navy, through Task Assignment RMMP-22-153/286-1/R001-06-01. The authors thank Manfred Cziesla for fruitful discussions during the course of this investigation and acknowledge the support given by J. G. Tuono and G. Tesi.

LITERATURE CITED

(1) Baroody, E.E., Wynne, J., Zimmer, M.F., U.S. Naval Propellant Plant, NavWeps Rept. 8686, Tech. Rept. 154, 1964.

(2) Cox, J.D., Head, A.J., Trans. Faraday Soc. 58, 1839-45, (1962).
(3) Crankankas, V., Aerojet-General Corp. Rept. No. 0235-01-7, Quarterly Report, 15 July 1960 (confidential).
(4) Good, W.D., Douslin, D.W., McCullough, J.P., J. Phys. Chem. 67, 1312-4 (1963).
(5) Good, W.D., Scott, D.W., Waddington, G., Ibid., 68, 1080 (1956).
(6) Graff, M., Cziesla, M., "Study of the Decomposition Mechanism of N-Fluoro-N-nitrobutylamines," U. S. Naval Propellant Plant, 1965, unpublished data.
(7) Graff, M., et al., NavWeps Rept. 8571, Tech. Rept. 147, 5 June 1964 (confidential).
(8) Hammond, J.E., Kordite Corp., Macedon, N. Y., private communication.
(9) "Handbook of Chemistry," N. A. Lang, Ed., 10th ed., McGraw-Hill, New York, 1961.
(10) "Handbook of Chemistry and Physics," 43rd ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1961.
(11) Ketelaar, J.A., "Chemical Constitution," p. 191, Elsevier Publishing Co., London, 1953.
(12) Klages, F., Chem. Ber. 82, 358, (1948).
(13) Lehmann, H., Ruschitzky, E., Chem. Tech. 16, 18, (1964).
(14) Marantz, Sidney, National Bureau of Standards, Washington, D. C., private communication.
(15) Rossini, F.D., "Experimental Thermochemistry," Vol. I, pp. 90, 107, Interscience, New York, 1962.
(16) Skinner, H.A., Ibid., Vol. II, pp. 25-8, 1962.
(17) Wilkins, R.L., "Theoretical Evaluation of Chemical Propellants," C.N. Besserer, F.E. Nixon, Eds., Prentice Hall, Englewood, N.J., 1963.
(18) Zimmer, M.F., Baroody, E.E., Schwartz, M., McAllister, M.P., J. Chem. Eng. Data 9, 527 (1964).

Alkyl Ethers

D. V. LOPIEKES

Boston Laboratory, Monsanto Research Corp., Everett, Mass.

A SERIES of ethers was obtained by the reaction of phenylmagnesium bromide, prepared commercially by the Arapahoe Chemical Co. as a 3M solution, with acetals above 100° C. in xylene according to a procedure of Kaye and Kogon (1). Table I summarizes the yield, boiling point, refractive index, and elemental analysis of the compounds prepared. The infrared spectra were consistent in each instance with the desired structure.

LITERATURE CITED

(1) Kaye, I.A., Kogon, I.V., J. Am. Chem. Soc. 73, 4893 (1951).

Table I. C_6H_5—CHCH$_2$—R'
                    |
                   OR

R	R'	B.P.[a] °C.	Mm.	Yield, %	n_D^r	Formula	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found
C$_2$H$_5$—	-N (ring)	70-72	0.14	47	1.5125^{25}	C$_{14}$H$_{21}$NO	77.0	77.5	9.7	9.4	6.3	6.4
C$_2$H$_5$—	—N(C$_2$H$_5$)$_2$	77-79	8.0	68	1.4872^{25}	C$_{14}$H$_{23}$NO	75.9	75.9	10.5	10.5	6.3	6.5
C$_2$H$_5$—	—OC$_6$H$_5$	106	0.04	40	1.5457^{25}	C$_{16}$H$_{18}$O$_2$	79.3	79.5	7.5	7.6	...	...
C$_2$H$_5$—	-N (ring with O)	82-86	0.05^b	50	1.5112^{20}	C$_{15}$H$_{23}$NO	77.2	77.0	9.9	10.0	6.0	5.9
C$_2$H$_5$—	-N (ring)	143-45	10.3^c	50	1.5070^{25}	C$_{14}$H$_{21}$NO$_2$	71.4	71.3	9.0	8.8	6.0	5.9

[a] Boiling points uncorrected. [b] Kaye and Kogon reported b.p. 135-47 ° C./9 mm.; yield, 62%. [c] Kaye and Kogon reported b.p. 134-36 ° C./ 10 mm.; yield, 23%.