temperatures of Smith is that prior to the 75°C withdrawal, two of his dilatometers leaked, leaving only four dilatometric measurements at 75° and 85°C. The recalculated Smith values are listed in the fourth column of Table VI. Similar criticism of the Owen et al. densities has been voiced by Kell and Whalley (*8*).

For the convenience of those workers requiring accurate densities of water between 0° and 80°C, a table of water densities calculated from Equation 5 is presented in Table VII. Although the densities in this table are quoted to the seventh decimal place, it should be realized that at least above 40°C they are uncertain in the sixth decimal place with the uncertainty increasing with temperature.

LITERATURE CITED

(1) Beattie, J. A., Blaisdell, B. E., Kaye, J., Gerry, H. T., Johnson, C. A., *Pro. Am. Acad. Arts Sci.*, **74**, 371 (1941).
(2) Chappuis, P., *Trav. Memoires Bur. Intern. Meas.*, **13**, C10 (1907).
(3) Chappuis, P., *ibid.*, D40 (1907).
(4) Gildseth, W. M., PhD Thesis, Iowa State University, 1964.
(5) Harned, H. S., Owen, B. B., "The Physical Chemistry of Electrolytic Solutions," 3rd ed., Reinhold, New York, N.Y., 1958.
(6) Jones, G., Taylor, E. F., Vogel, R. C., *J. Amer. Chem. Soc.*, **70**, 966 (1948).
(7) Kell, G. S., *J. Chem. Eng. Data*, **12**, 66 (1967).
(8) Kell, G. S., Whalley, E., *Phil. Trans. Roy. Soc.*, **258a**, 565 (1965).
(9) Owen, B. B., White, J. R., Smith, J. S., *J. Amer. Chem. Soc.*, **78**, 3561 (1956).
(10) Smith, J. S., PhD Thesis, Yale University, New Haven, Conn., 1944.
(11) Steckel, F., Szapiro, S., *Trans. Faraday Soc.*, **59**, 331 (1963).
(12) Tilton, L. W., Taylor, J. K., *J. Res. Nat. Bur. Stand.*, **18**, 205 (1937).

RECEIVED for review October 5, 1971. Accepted June 28, 1972. Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission (Contribution No. 3003), and some of the reduction of data was carried out at Augustana College, S.D. This paper is based in part on the PhD dissertation of W. M. Gildseth submitted to the Graduate Faculty of Iowa State University of Science and Technology, Ames, Iowa, in 1964. An independent part of these data was obtained by A. Habenschuss as part of his PhD dissertation.

Heat of Formation of Nitroxy Fluoride(G)

ROBERT T. REWICK,[1] RALPH ANDERSON, and RICHARD O. MacLAREN
United Technology Center, Division of United Aircraft Corp., Sunnyvale, CA 94088

The heat of the reaction $F_2(g) + NaNO_3(s) = O_2NOF(g) + NaF(s)$ has been measured calorimetrically, and from the resulting data, the standard heat of formation of $O_2NOF(g)$, $\Delta H_{f298}°$, has been established as +2.5 ± 0.5 kcal/mol.

Although the physical and chemical properties of nitroxy fluoride have been extensively studied, thermochemical data on the heat of formation of this potentially explosive O—F bonded species have not been published until recently. While work at United Technology Center on this subject was in process, Talakin et al. (*7*) reported a heat of formation of −4.2 ± 0.9 kcal/mol for gaseous O_2NOF at 21°C. However, bond energy estimates yielded a less exothermic value for the derived heat of formation of nitroxy fluoride than the value reported by the Russian workers, and one of the preliminary experimental approaches used in this work, which was similar to the one they used, produced inconsistent results. In an attempt to obtain a more accurate heat of formation value for nitroxy fluoride, which would be useful in describing the O—F bond energy in related compounds, a calorimetric program was selected to minimize side effects inherent in similar reactive systems.

EXPERIMENTAL APPROACH

Several possible reaction systems potentially applicable to the determination of the $\Delta H_{f298}°$ for $O_2NOF(g)$ by calorimetric methods have been reported. Each of the following systems was investigated to determine the most effective procedure. Preliminary emphasis was placed on the reproducibility of well-defined products from a simple reaction system which could be well characterized analytically.

The original preparation of nitroxy fluoride (*1*, *5*) involved the direct fluorination of nitric acid according to the following equation:

$$HNO_3(l,aq) + F_2(g) \rightarrow O_2NOF(g) + HF(g) \qquad (1)$$

In principle, Reaction 1 is ideally suited for calorimetric study; however, experimental difficulties associated with the degree of solubility of the reaction products in the nitric acid, and the application of the correct heat effect values for this process were found to limit the usefulness of this reaction for calorimetric study.

Skiens and Cady (*6*) have reported that the spark-induced decomposition of nitroxy fluoride yielded only nitrosyl fluoride and oxygen according to the following stoichiometry:

$$O_2NOF(g) \rightarrow NOF(g) + O_2(g) \qquad (2)$$

Because of the simple products, Reaction 2 appeared promising from a calorimetric standpoint. However, in tests employing nichrome fuse wire to initiate gas phase decomposition in a modified combustion bomb system, the reaction was more complex than previously reported, with variable formation of nitrogen dioxide, nitric oxide, and nitryl fluoride in conjunction with nitrosyl fluoride and oxygen.

Nitroxy fluoride has been reported (*1*) to decompose with aqueous potassium hydroxide:

$$O_2NOF(g) + 2OH^-(aq) \rightarrow {}^1/_2O_2(g) + F^-(aq) + NO_3^-(aq) + H_2O(l) \qquad (3)$$

The applicability of Reaction 3 was investigated by hydrolyzing

---

[1] Present address, Stanford Research Institute, Menlo Park, CA 94025. To whom correspondence should be addressed.

samples of pure nitroxy fluoride in 5*N* potassium hydroxide solution. Although stoichiometric quantities of fluoride ion and a decrease in alkalinity resulted from the chemical analysis of the subsequent solutions, the values obtained for the nitrate ion analysis were lower than expected. These results, in addition to an uncertainty in the application of correct heat of solution effects of the products in a calorimetric study, suggest that there might be errors inherent in the use of the alkaline hydrolysis reaction reported by the Russian workers (*7*) for the evaluation of the heat of formation of nitroxy fluoride.

The reaction of fluorine with solid anhydrous potassium nitrate has been reported (*3, 6, 8*) to yield nitroxy fluoride as the only gaseous products:

$$KNO_3(s) + F_2(g) \rightarrow O_2NOF(g) + KF(s) \qquad (4)$$

The reaction of fluorine with solid anhydrous sodium nitrate was expected to follow a similar course:

$$NaNO_3(s) + F_2(g) \rightarrow O_2NOF(g) + NaF(s) \qquad (5)$$

Synthesis of nitroxy fluoride by this method gave essentially theoretical yields. With an excess of finely divided anhydrous sodium nitrate and undiluted fluorine, yields of up to about 98% based on fluorine were realized. This system, because of its high yields, simplicity, and absence of detectable side reactions was chosen for the thermochemical evaluation of the heat of formation of nitroxy fluoride.

EXPERIMENTAL SECTION

Materials. Sodium nitrate was obtained in its highest commercial purity from the Mallinckrodt Chemical Co. and was used directly after drying for 8 hr at 125°C without further purification. Commercially available 98% purity fluorine, supplied by the Allied Chemical Co., was passed through a 200-cc $^3/_8$-in. o.d. copper coil cooled to liquid nitrogen temperature to remove hydrogen fluoride and other impurities, and then was stored in a volume-calibrated 5-liter stainless steel cylinder equipped with a pressure gauge. Residual amounts of air still present in the fluorine after cryogenic treatment were found to induce no detectable side reactions during fluorination.

Calorimeter. The basic apparatus used to measure the heat evolved from the reaction of fluorine and sodium nitrate was an all-metal flow calorimeter operated at 25°C and 1-atm pressure. The main calorimetric system consisted of a 15-cc U-tube reactor constructed from 12 in. of $^3/_8$-in. o.d. copper tubing. The reactor, after being packed with a weighed quantity of anhydrous sodium nitrate, was connected to the metal flow system and immersed in about 1600 cc of distilled water contained in a 2-liter Dewar flask having a tight-fitting $1^1/_2$-in. deep Styrofoam cover wrapped in aluminum foil. Extending through the insulating cover, in addition to the U-tube reactor, were a glass stirring rod, a Bureau of Standards calibrated Leeds and Northrup platinum resistance thermometer, and two quartz-encased calibration heaters.

Calibration. The heat capacity of the calorimetric system was evaluated by supplying a known quantity of electrical energy to the system during a measured time period through calibrated 12.25-Ω quartz heaters connected in parallel and by measuring the overall temperature rise with the platinum resistance thermometer. Because fixed quantities of the heat sink fluid were not monitored into the calorimeter during each experiment, the calibration was repeated after each run. To evaluate the accuracy limits of the electrical calibration method, the derived heat capacity value obtained by this procedure was compared to the value derived for the same system by the combustion of a National Bureau of Standards certified sample of benzoic acid in a standard Parr bomb. A difference in the two values of less than 0.5%, the combustion method giving the higher result, indicated the suitability of the electrical procedure.

Flow System. The entire flow system, with the exception of the copper U-tube reactor and a glass bubble counter and copper U-tube at the terminal end of the line, was constructed from $^1/_4$-in., 316 stainless steel tubing, Swagelok fittings, and number 2-VSR Whitey valves. A nitrogen supply line containing a molecular sieve drying column was connected in parallel with the calibrated 5-liter fluorine supply cylinder immediately preceding the U-tube reactor. In addition, the fluorine supply cylinder was equipped with a 760-1760 mm Heise gauge having 1-mm graduations. Immediately following the U-tube reactor in the flow system were three 60-cc packed (316 stainless steel Podbielniak Helipak) stainless steel traps in series, followed by a small glass bubble counter containing Kel-F oil. To prevent possible suck-back of Kel-F oil into the traps during a calorimetric run, a small copper U-tube cooled to liquid-oxygen temperature was installed between the last trap and the bubble counter. With appropriate valving, it was possible to isolate the trapping system from the rest of the line and evacuate it. A secondary line on the trapping system led to a calibrated 1.180-liter stainless steel volume into which products from the reaction between fluorine and sodium nitrate were allowed to gasify, and the pressure was determined with a 0-1000 mm Hg absolute Heise gauge capable of reading ±0.5 mm. The system also contained outlets for the connection of an infrared cell and a cylinder to determine the weight of the product.

Procedure. The weight of the copper U-tube reactor containing about 6 grams of dried reagent grade sodium nitrate was determined on a 1000-gram full-scale Mettler balance capable of reading ±1 mg. The reactor was connected to the flow system and enclosed in a 2-liter Dewar flask containing approximately 1600 cc of distilled water. The Styrofoam insulating cover containing the glass stirring rod, calibration heaters, and platinum resistance thermometer was carefully positioned on top of the Dewar flask. Stirring was commenced at a predetermined rate which minimized the time lag between the heat release period and the final drift rate equilibrium of the calorimetric determination.

Before initiating the reaction, the entire flow train was swept with a flow of dried nitrogen for 30 min, after which the traps were cooled to liquid-oxygen temperature, and the pressure in the system was carefully adjusted to 1 atm. The temperature of the heat sink fluid was then raised to 25°C with the calibration heaters, and the temperature was read with a platinum resistance thermometer and Mueller bridge. A nitrogen flow was again commenced through the system at a rate of about 50 cc/min, and the initial temperature drift-rate period of the calorimeter was determined for 15 min at 2-min intervals. After the nitrogen flow was terminated, fluorine was admitted to the flow system at the same rate, and the temperature of the calorimeter was determined as often as possible during the resulting heat-release period until a predetermined quantity of fluorine had passed through the sodium nitrate reaction bed as determined from the pressure drop in the fluorine storage tank.

Upon completion of the reaction, the system was flushed with nitrogen for 15 min while temperature readings were taken to obtain data for the final drift-rate period. The two sets of drift-rate temperature readings were fitted to straight lines by the method of least squares, and the true temperature rise for the reaction between fluorine and sodium nitrate was determined by subtracting from the observed equilibrium temperature rise a calorimeter heat-leak correction derived from the average slope of the two drift lines.

The nitrogen flush was then diverted around the trapping system, which was isolated and evacuated by a mechanical pump to a pressure of less than 50 μ, and the heat capacity of the calorimeter was evaluated by passing a known current for a measured time period through the 12.25-Ω calibration heaters. The final drift-rate period for the reaction between fluorine and sodium nitrate was used as the initial drift-rate period for the heat capacity determination. Temperature readings were plotted as previously described, and the heat capacity of the

Table I. Synthesis and Calorimetric Data for O_2NOF

	Run number						
	3[a]	5[a]	6[a]	7[b]	9[b]	10[b]	12[b]
Moles F_2 used	0.0576	0.0455	0.0489	0.0363	0.0139	0.0139	0.0134
F_2 flow rate ml/min	107	120	107	96	50	54	43
Moles O_2NOF formed							
Reactor wt loss	0.0284	0.0212	0.0271	0.0337	0.0130	0.0131	0.0126
Reactor analysis	0.0231	0.0226	0.0274	0.0336	0.0136	0.0135	0.0131
Gas pressure	...	0.0216	0.0272	0.0344	...	0.0131	0.0122
Gas wt	...	...	...	...	...	0.0134	0.0124
Av	0.0258	0.0218	0.0272	0.0339	0.0133	0.0133	0.0126
Percent conversion F_2 to O_2NOF							
Reactor wt loss	49.3	46.6	55.4	92.8	93.5	94.2	94.0
Reactor analysis	40.1	49.7	56.0	92.6	97.8	97.1	97.8
Gas pressure	...	47.5	55.6	94.8	...	94.2	91.0
Gas wt	...	...	...	...	...	96.4	92.5
Av	44.8	47.9	55.6	93.4	95.7	95.7	94.0
C_p calorimeter, cal/deg	1671	1672	1686	1675	1675	1716	1688
ΔT, °C	0.324	0.287	0.360	0.434	0.179	0.172	0.166
Q generated, cal	542	480	607	727	300	295	280
Av ΔH_{r298}°, kcal/mol	−21.0	−22.0	−22.3	−21.4	−22.6	−22.2	−22.2
Av ΔH_{f298}°, kcal/mol	+3.5	+2.5	+2.2	+3.1	+1.9	+2.3	+2.3

[a] Stoichiometric amounts of F_2 and $NaNO_3$. [b] Excess $NaNO_3$ (6 grams).

calorimeter was determined in terms of calories released per degree temperature rise.

The trapping system of the flow calorimeter was then warmed, and the condensed product from the reaction between fluorine and sodium nitrate was vacuum transferred to the calibrated 1.180-liter measuring volume; the pressure was determined with the 0–1000-mm Hg absolute Heise gauge. From the known volume, temperature, and pressure of the measuring system, the number of moles of gaseous product was computed. The average molecular weight of the product, determined by weighing the material to an accuracy of ±1 mg, differed from the calculated molecular weight of nitroxy fluoride by about 0.5%.

A spectral analysis of the generated nitroxy fluoride product in a 10-cm. stainless steel infrared cell equipped with sodium chloride windows indicated no impurities, and was in good agreement with the reported spectrum (*6*).

Upon completion of each calorimetric determination, the U-tube reactor was again weighed, and the contents were accurately analyzed by a modified null-point potentiometric method (*2*) for the fluoride content generated from the nitroxy fluoride synthesis reaction.

Fundamental Quantities. The defined calorie equal to 4.1840 absolute joules was used in the evaluation of the energy equivalent of the calorimeter. The molecular weights for all materials were based on the 1961 atomic weight scale. To derive the heat of formation of nitroxy fluoride from the experimentally observed heat of Reaction 5, the following standard heats of formation at 298K were employed: $NaNO_3$(s), −111.54 kcal/mol, and NaF(s), −136.0 kcal/mol (*4*).

RESULTS AND DISCUSSION

Synthesis and calorimetric data for several experiments are presented in Table I. For each experiment, the number of moles of nitroxy fluoride used in the calculations is an average value derived from several independent measurements.

The reactor weight-loss data can be correlated with the formation of nitroxy fluoride by examining the stoichiometry of Reaction 5, in which a solid phase weight loss of 1 gram should be equivalent to the formation of 23.3 mmol of nitroxy fluoride and sodium fluoride. Good agreement was found in the quantity and purity of the nitroxy fluoride generated in the several calorimetric studies.

The percent conversion of F_2 to O_2NOF appeared to be a function of the F_2 flow rate and the amount of $NaNO_3$ used in the run (Table I). The conversion was nearly doubled by using excess $NaNO_3$; a reduction in the flow rate had only a small effect on the percent conversion.

The N_2 flow rate used under calibration conditions was always adjusted as close as possible to the F_2 flow rate used during the reaction with $NaNO_3$. The derived heat of formation value of nitroxy fluoride did not appear to be a function of the fluorine flow rate, which was varied between 120 and 43 ml/min.

Because of the large size (5 liters) of the fluorine storage tank, the pressure drops that occurred as the desired quantity of the gas was supplied to the reaction system were small enough to minimize the Joule-Thomson effect, and in addition made it relatively easy to maintain atmospheric pressure in the flow system.

To minimize heat leak corrections in the evaluation of the heat of formation of nitroxy fluoride, the only portion of the flow system constructed from copper was the U-tube reactor completely submerged in the calorimeter heat sink fluid. In addition, the calorimetric fluid was stirred at such a rate that the time lag between the heat-release period of the determination and the attainment of the final drift-rate equilibrium was less than 2 min.

Within the accuracy limits inherent in the calibration procedure and the weighing, pressure determination, and analytical methods, the average experimentally determined standard heat of reaction of fluorine and sodium nitrate is −22.0 ± 0.5 kcal/mol. By use of this value and the reported standard heats of formation (*4*) of sodium nitrate and sodium fluoride, the standard heat of formation per mole of nitroxy fluoride is found from the following relationship:

$$\Delta H_{f298}^\circ \ O_2NOF(g) = 24.5 + \Delta H_{r298}^\circ \text{ kcal/mol} \qquad (6)$$

to be +2.5 ± 0.5 kcal/mol.

The absence of detectable side reactions, the purity of the nitroxy fluoride product, and the independent checks on the amount of product generated, as well as the essentially constant derived heat of formation value under varied flow conditions, corroborate the validity of the above results.

LITERATURE CITED

(1) Cady, G. H., *J. Amer. Chem. Soc.*, **56**, 2635 (1934).
(2) O'Donnell, T. A., Stewart, D. F., *Anal. Chem.*, **33**, 337 (1961).
(3) Pauling, L., Brockway, L. O., *J. Amer. Chem. Soc.*, **59**, 13 (1937).

(4) Rossini, F. D., Wagman, D. D., Evans, W. H., Levine, S., Jaffe, I., "Selected Values of Chemical Thermodynamic Properties," *Circ.* 500 of the National Bur Standards, U.S. Government Printing Office, Washington, DC, 1952.
(5) Ruff, O., Kwasnik, W' *Z. Angew. Chem.*, **48**, 238 (1935).
(6) Skiens, W. E., Cady, G. H., *J. Amer. Chem. Soc.*, **80**, 5640 (1958).
(7) Talakin, O. G., Akhanshchikova, L. A., Sosnovskii, E. N., *Zh. Fiz. Khim.*, **36**, 1065 (1962).
(8) Yost, D. M., Beerbower, A., *J. Amer. Chem. Soc.*, **57**, 782 (1935).

Received for review December 27, 1971. Accepted April 3, 1972. This work was supported financially through a contract administered by the Office of Naval Research under Contract No. 3433(00), Washington, DC.

Liquid Thermal Conductivities of Organic Compounds and Petroleum Fractions

GEORGE M. MALLAN,[1] MARSHALL S. MICHAELIAN,[2] and FRANK J. LOCKHART[3]
Department of Chemical Engineering, University of Southern California, Los Angeles, Calif. 90007

Liquid thermal conductivities of 29 organic compounds and 15 petroleum fractions have been measured in a transient, relative apparatus of the hot wire type between 20° and 120°C at a pressure of 7.5 atm.

Liquid thermal conductivity is a physical property difficult to measure accurately. Natural convection caused by the imposed temperature difference tends to make experimental values too high. It is known now that many data in reference books and handbooks are in error on the high side by 20% or more.

Of all organic compounds, toluene has been the one studied most for thermal conductivity. It is instructive to note how the experimental values of *k* have changed over the past 40-odd years, as shown in Table I. The decrease is due to improvements in instrumentation and experimental techniques. Figure 1 shows the data graphically and emphasizes that at the present time there is no assurance that future measurements will not give even lower values. Thermal conductivity measurements for other organic compounds show similar variations over the years.

This paper reports thermal conductivities of 29 organic compounds and 15 petroleum fractions as a function of temperature, determined experimentally in relative, transient equipment.

Table I. Thermal Conductivity of Liquid Toluene at 20°C

Year	Observers	Method[a]	*k*, *W/m* °C
1923	Bridgman (*2*)	CSA	0.1547
1924	Rice (*14*)	CSR	0.1414
1930	Smith (*19*)	CSA	0.1488
1931	Shiba (*18*)	PIEZO	0.1469
1934	Kardos (*11*)	WSR	0.1450
1949	Abas-Zade (*1*)	WSA	0.1395
1951	Riedel (*15*)	C-P-S, SA	0.1360
1954	Schmidt, Leidenfrost (*17*)	CSA	0.1362
1956	Challoner, Powell (*4*)	PSA	0.1378
1956	Frontasev (*5*)	PSA	0.1364
1957	Vargaftik (*21*)	WSA	0.1347
1957	Briggs (*3*)	CSR	0.1364
1959	McCready (*12*)	CSA	0.1386
1959	Frontasev, Gusakov (*6*)	PSA	0.1359
1961	Ziebland (*23*)	CSA	0.1343
1963	Jamieson, Tudhope (*9*)	WSA	0.1338
1963	Horrocks, McLaughlin (*8*)	WTA	0.1345
1965	Venart (*22*)	CSA	0.1327
1967	Poltz, Jugel (*13*)	PSA	0.1306

[a] Method:
C = cylinders S = steady state A = absolute
W = wire T = transient R = relative
P = plates
S = spheres

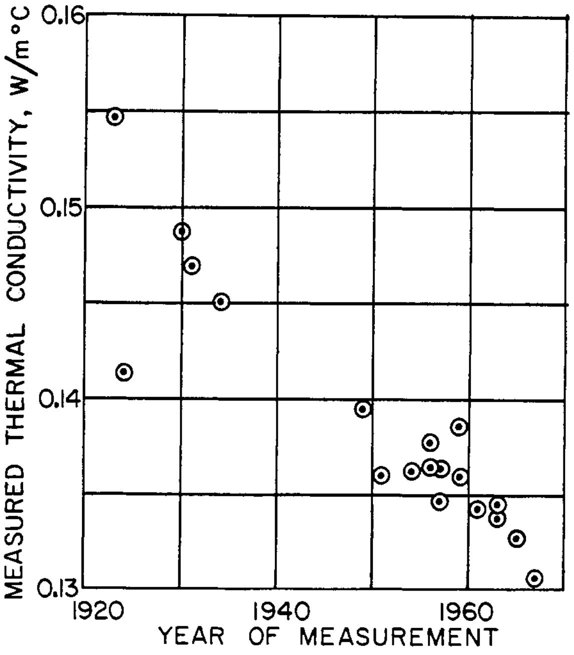

Figure 1. Thermal conductivity at 20°C of liquid toluene

---

[1] Present address, Garrett Research and Development Co., Inc., La Verne, Calif.
[2] Present address, Chevron Research Corp., Richmond, Calif.
[3] To whom correspondence should be addressed.