The enthalpy change for the reaction is

$$\Delta H = \Delta H_f(CH_3ONO_2) + 20.537$$

The measured heat evolution in kcal. per mole of methyl nitrate formed is given by

$$\Delta Q = \frac{\text{(calorimeter constant)}}{\text{(moles of } CH_3ONO_2)} \text{(temp. rise)} = \frac{(0.1684)(0.070)}{(0.00111)} = -10.620$$

This measured heat evolution is equal to the change in internal energy of the reaction plus an additional heat evolution due to the expansion of the two gases into the bottle. Thus

$$\Delta Q = \Delta E - (n_{N_2O_5} + n_{CH_3ONO_2})RT$$

$$\Delta Q = \Delta H - 1.958 \text{ kcal./mole}$$

$$-10.620 = \Delta Q = \Delta H_f(CH_3ONO_2) + 20.537 - 1.958 \text{ kcal./mole}$$

The heat of formation of methyl nitrate from the elements at 25° as the hypothetical gas at 1 atmosphere pressure is

$$\Delta H_f(CH_3ONO_2) = -29.2 \pm 0.3 \text{ kcal./mole (exothermic)}$$

The thermodynamic data used in the above calculations are given in Table I below. All values refer to the gases at 25° and 1 atmosphere pressure.

TABLE I

SUMMARY OF THERMODYNAMIC DATA USED IN THIS PAPER

	NO_2	N_2O_4	N_2O_5	CH_3ONO	CH_3ONO_2
$H^0_{298.16}$	7.964[5]	2.239[5]	3.17[3]	−16.27[6]	−29.2
$S^0_{298.16}$	57.47[5]	72.73[5]	82[8]	67.84[6]	80.97[7]

The thermal data for methyl nitrite in Table I based on the equilibrium between gaseous methyl nitrite, hydrogen chloride, methyl alcohol and nitrosyl chloride which was studied by Leermakers and Ramsperger[6] have been recalculated on the basis of the more modern value for the heat of formation of hydrogen chloride given by Rossini, Wagman, Evans, Levine and Jaffe,[9] and the thermodynamic data of nitrosyl chloride given by Beeson and Yost.[10] The recalculated entropy for methyl nitrite, 67.84, is to be compared with that for nitromethane, 63.82. It is to be expected that the lower symmetry and, as shown by Piette, *et al.*,[11] and D'Or and Tarte[12] the coexistence of approximately equal amounts of *cis* and *trans* isomers of methyl nitrite should result in an entropy higher by about three entropy units than that of nitromethane, whereas the entropy given in the original paper was only 0.58 e.u. higher. Thus, the direction of the correction is as should be expected.

Discussion of Results

The value for the heat of formation of methyl nitrate found in this paper, −29.2 ± 0.3 kcal./mole, may be compared to that found from the heat of explosion of the liquid as observed by Whittaker, Wheeler and Pike.[13] This value, combined with the heat of vaporization given by McKinley-McKee and Moelwyn-Hughes[14] gives for the heat of formation of gaseous methyl nitrate from the elements at 25° and one atmosphere pressure, −29.4 ± 0.8 kcal./mole, in excellent agreement with the value found in this paper from a completely different reaction involving gaseous instead of liquid methyl nitrate.

Of interest in kinetic studies, thermal data for reactions (1) and (2) were calculated.

$$CH_3ONO + 1/2\ O_2 = CH_3ONO_2$$
$$\Delta H = -12.93 \text{ kcal.}, K_{298} = 3.62 \times 10^7 \text{ atm.}^{-1/2} \quad (1)$$

$$CH_3ONO + NO_2 = CH_3ONO_2 + NO$$
$$\Delta H = +0.706 \text{ kcal.}, K_{298} = 6.17 \quad (2)$$

The enthalpy change for reaction 1 may be compared to the value −10.3 kcal. for the analogous reaction of the ethyl homologs. Since in the course of an hour, no nitric oxide band could be observed in the infrared spectrum of a mixture of methyl nitrite and nitrogen dioxide, it is concluded that reaction 2 is not active in the reaction between nitrogen pentoxide and methyl nitrite.

The present thermodynamic data are compatible with the assignment of *cis-trans* isomerism to the double methyl proton nuclear magnetic responance spectrum reported by Piette, Ray and Ogg[11] for methyl nitrite. The N^{14} resonance spectrum (to be displayed in a subsequent publication) is extremely broad ($\Delta W_{1/2}$ = 200 p.p.m. at 2.88 megacycles). The dynamic process involved in the rotational isomerism is expected to cause this great enhancement of the electric quadrupole relaxation of the N^{14} nucleus.

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THE THERMAL DECOMPOSITION OF SOLID SILVER METHYL AND SILVER ETHYL[1]

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This work was undertaken to investigate the potentialities of silver alkyls as low temperature gas phase sources of alkyl radicals according to the reaction, Solid (I) = Solid (II) + Gas. Semerano[2] studied the decomposition of silver alkyls below 0°. On heating wet (under alcohol) or moist silver methyl precipitate it decomposed to ethane and silver. Silver ethyl was reported to yield butane, ethylene and ethane. Semerano suggested the use of these compounds as sources of alkyl radicals. Bawn and Whitby[3] studied the decomposition of dissolved silver methyl and proposed that the decomposition proceeded through methyl radicals, although objection has been made to this interpretation.[3] Support for free radical mechanisms has been found in the decomposition of silver

(1) This work was supported by the Office of Naval Research.

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phenyl in solution,[4] and of silver isobutenyl precipitate under alcohol.[5]

In the present study, the decomposition of the dry alkyls has been investigated. The work proved more difficult than anticipated and the results (reproducibility, nature of samples, etc.) leave something to be desired. Certain aspects of interest appear worthy of report.

Experimental

Lead tetramethyl and lead tetraethyl were purified by distillation. The reactor consisted of a cylindrical tube 50 cc. in volume, fitted with a taper joint at the top and having a short tubular (area 0.75 cm.^{2}) extension with flat bottom at the lower extremity.

Twenty ml. of 1.2% silver nitrate methanol solution and 0.06 g. of lead tetramethyl in 15 ml. of methanol were cooled to −78° in a dry box. The solutions were mixed in the reactor which was then stoppered, and the yellow silver methyl precipitate was centrifuged at −78°. The precipitate deposited as a thin layer on the flat bottom of the reactor well. The methanol was siphoned off, 10 ml. of dimethyl ether at −78° was added and the precipitate stirred with a rod. The suspension was again centrifuged at −78°. All operations were performed under nitrogen. Seven washings removed methanol sufficiently to allow the reactor (with the well at −78°) to be evacuated below 10^{-3} mm. by pumping (3–15 hours). In this process the silver methyl wafer ($\sim$0.1 mm. thick) curled and cracked a little.

Red-brown silver ethyl was prepared in like manner.

To initiate decomposition, the −78° bath was replaced by a thermostat so that the reactor well and silver alkyl wafer were submerged. Temperature was constant to within 0.1°. Decomposition was followed by pressure change. Gas products were analyzed on a Consolidated 21-102 mass spectrograph.

Results and Discussion

Products of Decomposition.—Mass spectrographic analysis of the gas product (after warming the residue to room temperature) from silver methyl showed ethane, with 12% dimethyl ether, 1% methanol and some water. Although the original precipitate was pumped extensively at −78°, several mm. vapor of methanol, and some dimethyl ether and water were always left. Most of the methanol and water entered the gas phase only after warming the residue. Analysis of the silver residue showed $\sim$13% $AgNO_3$; no lead was found. With silver ethyl, the product gas was butane, with possible small amounts of ethane and ethylene; the silver residue contained $\sim$7% $AgNO_3$.

X-Ray diffraction patterns of the residue were identical with those of bulk silver powder, even when the residue was kept at reaction temperature. The sharpness of the pattern lines suggested particle diameter between 10^{-5} to 10^{-3} cm. No success was had in obtaining silver alkyl patterns.

The decomposition of silver ethyl was conveniently measurable at slightly lower temperature ($> -38°$) than for silver methyl ($> -30°$). Excessive heating in both cases gave rise to explosions or occasional deflagration.

Form of the Decomposition Rate Curve.—For both silver methyl and silver ethyl, after an initial (2–15% reaction) rapid pressure increase accompanied by some browning (and followed sometimes by a short induction period), the rate of pressure increase was constant and changed quite sharply to zero near 100% decomposition. On the average, the rate was constant over the middle 80% decomposition and, neglecting the initial rapid pressure rise, was "zero order" over more than 90% of the reaction. Early work with a sample of lead tetramethyl from the Ethyl Corporation, used without any additional purification, gave rise to sigmoid decomposition pressure curves. These were never found using the compound prepared and purified by us, although an occasional run might bend a little from a straight line.[6] The rate of decomposition (slope) was not reproducible with different preparations of silver alkyl and varied several fold.

Cooling.—Interruption of reaction by freezing to −80° did not affect the subsequent decomposition rate on returning to the reaction temperature.

Addends.—Nitric oxide, oxygen, dimethyl ether or methanol gas, added during the middle of a run, were without effect on the rate. Preparations of silver methyl where excess silver nitrate or silver powder were added showed no apparent effect. Removal of gas products at a certain point during a run did not affect the subsequent rate.

Effect of Temperature.—Since rates were not reproducible between different samples, experiments were done in which, during the constant portion of the rate behavior, the initial temperature was raised 3–5° (and then sometimes lowered again), or the initial temperature was lowered (and then sometimes raised). Activation energies for both alkyls ranged around 35 ± 12 kcal. The occurrence of such large activation energies at the low temperatures employed signifies an abnormally large frequency factor. There was some indication that the heating–cooling cycle ($T_1 \rightarrow T_2 \rightarrow T_1$) was not reversible and that the final rate on reversion to T_1 was less than the original.

Remarks.—The decomposition of both alkyls evidently occurs by similar mechanisms. An adequate account must be compatible with the observed rate behavior and high frequency factor. Solid reactions have been customarily attributed to reaction at constant surface area, while high frequency factors have been attributed to layer or mosaic block decomposition.[6] In this case, the extreme range of reaction for which the constant rate holds would demand that the precipitate particles be *monodisperse*, while the decomposition of mosaic block or layers might be expected to lead to explosion in this exothermic reaction. Any process involving the propagation of a constant number of reactive sites would account for the rate behavior.

The initial rapid pressure rise was at least in part due to solvent release on warming to reaction temperature. In any case, the occurrence (sometimes) of a later short induction period signifies that the initial process is not directly related to the main process.

The lack of effect of nitric oxide and oxygen shows that free radicals do not enter the gas phase and that free radicals as such are not present in the solid.

Acknowledgment.—We thank Professor E. C.

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(6) *Cf.* W. E. Garner, "Chemistry of the Solid State," Butterworth Scientific Publications, London, 1955; see p. 233, Fig. Ia and shape of lead azide curves.

Lingafelter for his kind coöperation in the use of the X-ray diffraction equipment and for an estimate of particle size. We thank the Ethyl Corporation for a gift of chemicals.

THERMODYNAMICS OF THE DISPROPORTIONATION OF TITANIUM TRIBROMIDE

By Elton H. Hall and John M. Blocher, Jr.

Contribution from Battelle Memorial Institute, Columbus, Ohio

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As a means of obtaining the thermodynamic properties of $TiBr_2$ from published data for $TiBr_4$ and $TiBr_3$, the disproportionation equilibrium (1) has been studied

$$2TiBr_3(s) = TiBr_4(g) + TiBr_2(s) \qquad (1)$$

The partial pressure of $TiBr_4(g)$ was found to vary with the composition of the solid phase at constant temperature indicating that solid solubility occurs between $TiBr_3$ and $TiBr_2$. In fact, the variation was so much greater than in the corresponding $TiCl_3$ disproportionation[1-3] that the effects of solid solubility could not be neglected.

When the magnitude of the task of defining this system became apparent, it was decided that the results would not justify the expense, and the work was concluded. However incomplete, the data lead to a value for the heat of formation of $TiBr_2$ which is thought to be the best currently available.

Experimental

Titanium tribromide was prepared by reduction of distilled $TiBr_4$ with iodide-process titanium, and sublimation under the equilibrium pressure of $TiBr_4$. Chemical analysis of one such sample gave Ti, 16.9% and Br, 83.6%, corresponding to $TiBr_{2.97}$. The deviation from $TiBr_3$ is within the uncertainty of the analysis. For the purpose of later calculations, the composition $TiBr_3$ was assumed.

The pressures were measured with a null-indicating quartz Bourdon gage heated in an air-bath thermostat (±0.4°). After the pressure data were obtained over $TiBr_3$, a Willard valve[4] was opened and some $TiBr_4$ was pumped into a demountable cold trap. The composition of the residual solid phase was calculated from the original weight of the $TiBr_3$ and the weight of $TiBr_4$ removed. Pressure data then were observed on the new composition. In this manner, the data of Fig. 1 were obtained at five different compositions ranging from $TiBr_3$ to $TiBr_{2.65}$. In addition, measurements were made on a sample of uncertain composition near $TiBr_2$ which was prepared by the reduction of $TiBr_4$ with excess titanium. Since $TiBr_3$ is slightly volatile in the temperature range employed, the observed total pressure must be corrected to obtain the partial pressure of $TiBr_4(g)$. In order to make this correction, preliminary data were obtained[5] for the vapor pressure of $TiBr_3$ which may be represented by the equation

$$\log P_{\text{mm}} = -8930/T + 11.6 \qquad (2)$$

While this equation must be considered tentative, it is adequate for the present purpose since the correction amounts to a small fraction of the total pressure.

Discussion

Since the activities of $TiBr_3$ and $TiBr_2$ in the solid phase are not available, the equilibrium constant cannot be calculated directly from the observed $TiBr_4$ pressure at a given composition. Therefore, an alternative treatment was employed.

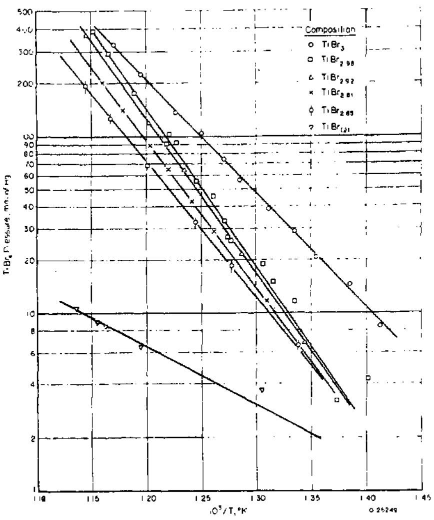

Fig. 1.—Disproportionation pressure of $TiBr_3$.

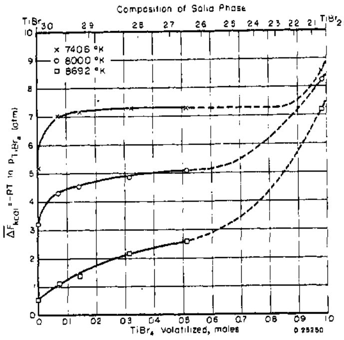

Fig. 2.—Partial molal free-energy isotherms.

The free energy change for converting 2 moles of $TiBr_3(s)$ to 1 mole of $TiBr_2(s)$ and 1 mole of $TiBr_4$(g, 1 atm.) is, by definition, the standard free-energy change, $\Delta F^0{}_1$, for reaction 1. If no solid solubility existed, the equilibrium pressure, P_{TiBr_4}, would remain constant with composition as defined by $\Delta F^0{}_1 = -RT \ln P_{TiBr_4}$. With solid solution present, P_{TiBr_4} varies with the composition of the solid phase, and $dF/dN = \Delta\bar{F} = -RT \ln P_{TiBr_4}$, where dF is the free energy change for removal of dN mole of $TiBr_4$ at equilibrium and compressing it to 1 atm. As $TiBr_4$ is removed incrementally in converting the solid phase from 2 moles of $TiBr_3(s)$ to 1 mole of $TiBr_2$

$$\int_0^1 \Delta\bar{F}\, dN = \Delta F^0{}_1$$

since the difference in free energies of the initial and final states of the system must be equal regardless of the path taken.

Except for the points at the uncertain composition near $TiBr_2$, the available data are limited to the $TiBr_3$ side of the system. Therefore, in compensating for this deficiency, the estimated standard entropy change for reaction 1 was used to establish the shape of the $\Delta\bar{F}$ curves. The entropies are given in Table I together with the heat capacities used for extrapolation.

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