three equations in the three unknowns, a, b and d. It has been our practice to use ten points for eq. 7 and 8 (7 degrees of freedom) and eighteen to twenty points for eq. 3. The result of such an adjustment is given in the last column of Table I. The three equations at the foot of the table give an illustration of the rapidity of convergence. Usually a three parameter equation such as eq. 8 requires only a single adjustment if the original value for c is in error by no more than 10%.

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The Thermal Decomposition of Nitrate Esters. III. *n*-Propyl Nitrate[1]

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Previous papers in this series[2,3] have described a study of the thermal decomposition of ethyl nitrate using the infrared spectrometer as an analytical tool. The thermal decomposition of *n*-propyl nitrate has been examined in the same way and the results are reported here.

Experimental

The details of experimental procedure were the same as those used earlier.[2] *n*-Propyl nitrate was prepared from nitric acid and *n*-propyl alcohol. It was vacuum distilled at 150 mm. and a middle fraction taken. *n*-Propyl nitrite was prepared from nitrous acid and *n*-propanol, distilled and the fraction boiling at 56–58° used.

Results

The results obtained by the decomposition of samples of *n*-propyl nitrate at 191° for varying periods of time are shown in Table I. The initial pressures of *n*-propyl nitrate were of the order of 20 mm. Analyses for the *n*-propyl nitrate, *n*-propyl nitrite and nitroethane were made using the infrared absorption peaks at 11.68, 12.55 and 6.31 μ, respectively. Nitrogen dioxide and nitric oxide were analyzed colorimetrically as before.[2] The presence of formaldehyde in the products was indicated by its odor and by the deposition of a white deposit assumed to be paraformaldehyde[4] on the reaction bulb walls. No analyses were carried out for it however.

The effect of various additives on the rate of reaction and on the product distribution is shown in Table II.

TABLE I

THE THERMAL DECOMPOSITION OF *n*-PROPYL NITRATE AT 181°[b]

Moles per mole of *n*-propyl nitrate initially present.

Time, min.	*n*-Propyl nitrate	*n*-Propyl nitrite	Nitroethane	Nitrogen dioxide	Nitric oxide	Total nitrogen	10^5k[a] sec.$^{-1}$
3.80	0.767	0.064	0.100	0.014	0.041	0.985	115
7.57	.581	.150	.164	.018	.059	0.973	119
10.55	.455	.249	.191	.040	.062	1.008	124
15.10	.371	.300	.263	.042	.070	1.048	110
22.57	.192	.380	.314	.042	.131	1.060	122
30.06	.122	.427	.324	.098	.103	1.078	117
50.10	.028	.455	.357	.014	.131	0.985	122
60.01	.005	.433	.404	.010	.149	1.000	
75.00	.005	.420	.400	.020	.275	1.120	

$^{b}10^5k_{\text{av.}} = 118$

Av. dev. = 4

[a] First-order rate constant. [b] From the data obtained manometrically by Phillips[5] the rate constant calculated at this temperature was 0.00093 sec.$^{-1}$

TABLE II

THE EFFECT OF ADDITIVES ON THE THERMAL DECOMPOSITION OF *n*-PROPYL NITRATE AT 181°

		Initial pressure (mm.)				Yield,[a] %	
Expt.	Additive	$C_3H_7NO_3$	Additive	Time, min.	Reaction, %	C_3H_7ONO	$C_2H_5NO_2$
1	..	22.5	..	10.6	52.5	47.4	36.4
2	NO_2	22.0	18.1	30.0	54.0	84.0	23.4
3	O_2	22.2	32.0	30.1	33.3	23.0	52.6
4	O_2	18.5	70.2	60.7	39.4	20.5	42.5
6	NO	22.8	23.3	10.0	52.2	97.5	10.9
7	NO	22.5	50.1	10.0	55.0	100.0	4.8

[a] The fact that the yields exceed 100% for runs 2, 6 and 7 is attributed to the experimental error of the analysis.

Discussion

The above reaction products are analogous to those found for the ethyl nitrate decomposition and fit in well with the mechanism proposed.[2] The *n*-propyl nitrate case differs from the ethyl nitrate case in that (a) the nitro compound is a much more important product and (b) the kinetics obey a simple first-order law and are virtually unaffected by the addition of substantial amounts of nitric oxide (expts. 1, 6 and 7 of Table II). Both of these differences may be attributed to the fact that the *n*-propoxyl radical is less stable than the ethoxyl radical toward decomposition *via*

$$RCH_2O\cdot \longrightarrow R\cdot + CH_2O$$

This is in line with the general effect of structure on the stability of these radicals.[6]

The effects of the additives on the product distribution offer further support for the reaction mechanism.[2] The effect of added nitric oxide in boosting the yield of *n*-propyl nitrite at the expense of nitroethane is especially striking. The similar effect of nitrogen dioxide probably arises *via* its reduction to nitric oxide. The increase in the nitroethane yield at the expense of the *n*-propyl nitrite effected by the addition of oxygen may be explained by the oxidation of some of the nitrite ester back to the nitrate ester by the oxygen and the nitrogen dioxide formed in the decomposition. Ogg[7] has shown that ethyl nitrite is converted to ethyl nitrate by a mixture of nitrogen dioxide and oxygen although neither oxidant is effective alone.

The explanation of the effect of the additives on the kinetics follows that used for the ethyl nitrate case.[3]

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[1] Full experimental details of this work including infrared spectra can be found in the reference, J. B. Levy and F. J. Adrian, Navord, 2608, 1952.

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[5] L. Phillips, Thesis, University of London, 1949.

[6] F. F. Rust, F. H. Seubold, Jr., and W. E. Vaughan, THIS JOURNAL, **72**, 338 (1950).

[7] R. A. Ogg, Jr., at "The Chemistry of the Oxides of Nitrogen," symposium sponsored by the Office of Ordnance Research, Chicago Illinois, September 3 and 4, 1953.

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Melting Point of Carbon Tetrachloride

BY A. K. DUNLOP

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An incidental determination of the melting point of carbon tetrachloride gave a result appreciably higher than previously published values.

The carbon tetrachloride used was a heart cut, b.p. 76.8°, obtained by distilling Baker Analyzed product through a 40-plate Oldershaw column at 20:1 reflux ratio. The purity of the heart cut, determined independently in a 5-ml. calorimeter,[1] was found to be 99.98 mole %. A calorimeter, similar to that employed by Rossini,[2] containing a 50-ml. sample, and a 25 ohm platinum resistance thermometer calibrated two months previously by the National Bureau of Standards were used in the melting point determination.

The data obtained on two separate samples are given in Table I along with previous literature values.

TABLE I

MELTING POINT OF CARBON TETRACHLORIDE

Sample 1, m.p. °C.	−22.782°
Sample 2, m.p., °C.	−22.782
Sample 2, f.p., °C.	−22.796, −22.793
Average	−22.788
Corr. for impurity	+ 0.036
Final value	−22.75 ± 0.03°
Timmermans, Martin[3]	−22.95
Skau[4]	−22.85
Johnston, Long[5]	−22.87
Deffet[6]	−22.95
Stull[7]	−22.79
Staveley, Gupta[8]	−22.96

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[1] D. D. Tunnicliff and Henry Stone, *Anal. Chem.*, **25**, 73 (1955).

[2] A. R. Glasgow, Jr., A. J. Streiff and F. D. Rossini, *J. Research Natl. Bur. Standards*, **35**, 355 (1945).

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The Preparation of Fluorocarbon Carboxylic Acid Cyanide Dimers

BY R. H. PATTON AND J. H. SIMONS

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It has been found that fluorocarbon carboxylic acid chlorides react readily with silver cyanide to yield a new fluorocarbon derivative.

These new cyanide derivatives are readily hydrolyzed by water and alcohols to yield, respectively, acids and esters plus hydrogen cyanide. They also react vigorously with silver fluoride or mercuric fluoride to yield the acid fluoride of the original fluorocarbon carboxylic acid and silver or mercuric cyanide.

A few of the physical properties of these compounds are given in Table I.

The determined molecular weights of these compounds as well as the fact that they are independent of pressure at constant temperature indicate that the substances exist in the vapor as "dimers" of the simple formulas. The analogous organic compounds are known to exist in two forms convertible one into the other. For example, the first member of the series[1]

$$2CH_3COCN \longrightarrow CH_3COOC(CN)_2CH_3$$

where the monomer has a boiling point of 93° and the dimer 210°. Melting point of the dimer is 69°. It is obvious that the fluorocarbon derivatives are different from the organic ones as the monomer was not obtained, the vapor density indicates no equilibrium between monomer and dimer, and the reaction with water and metallic fluorides produces either the parent acid or acid fluoride. Although the molecular weights indicate the compounds to be non-reversible dimers, the chemical reactions indicate that these do not have structures analogous to the organic analogs.

TABLE I

Compound	B.p., °C.	d^{25}_4	CN anal., % Theory	CN anal., % Found	Mol. wt. of vapor dimer Theory	Mol. wt. of vapor dimer Found
$(CF_3COCN)_2$	83–84	1.440	21.14	20.92	246	246
$(CF_3CF_2COCN)_2$	106–108	1.532	15.03	14.77	346	346
$(CF_3(CF_2)_2COCN)_2$	136–138	1.606	11.66	11.52	446	444
$(CF_3(CF_2)_4COCN)_2$	190–193	1.719	8.05	7.63	646	..

Since all of these compounds were prepared by the same method, the preparation of the dimer of trifluoroacetyl cyanide will serve as an example. The only difference among the preparations was the reaction time, which ranged from three days for the first member to three weeks for the last member.

Experimental

Trifluoroacetyl Cyanide Dimer.—Approximately 0.05 mole of trifluoroacetyl chloride was transferred to a heavy-wall glass vial containing 10.7 g. (0.08 mole) of dry silver cyanide. The vial was sealed and placed in a water-bath for three days with the temperature maintained at 80–95°. The vial was then cooled in liquid air, opened and attached to a vacuum manifold system and the contents transferred to another vial. The second vial was then removed from the manifold system and the contents transferred to a small fractionating apparatus, avoiding as much as possible contact with atmospheric moisture. The product was then fractionated. The yield of colorless, mobile liquid, b.p. 83–84°, was 5.0 g. (0.04 mole).

Analysis.—Since these compounds hydrolyze readily in water, advantage was taken of this by using the usual gravimetric cyanide analysis of the hydrolyzed solution of these compounds.

Vapor Density.—The molecular weight in the vapor was calculated by measurements of the vapor density. This was done by weighing a known volume of the gas at a known temperature and pressure. A bulb of measured volume carrying a stopcock and ground joint was attached to a vacuum system, exhausted, and filled with the gas under investigation at a measured pressure and temperature. The bulb was then removed and weighed. Table II shows the molecular weight of the methforyl compound at constant temperature with varying pressure.

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[1] H. Hubner, *Ann.*, **120**, 335 (1861).