Thermal Decomposition of Ketoxime Carbamates: An Investigation of the Thermolysis of Thiofanox

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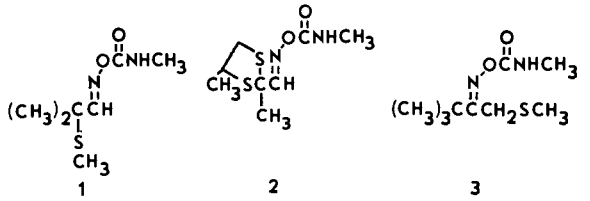
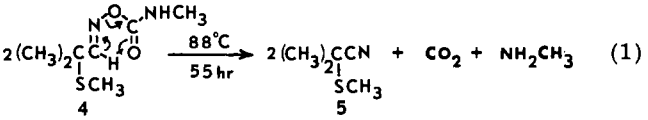
The thermal decomposition of thiofanox, 3,3-dimethyl-1-(methylthio)-2-butanone *O*-[(methylamino)-carbonyl]oxime (**3**), is investigated. The thermolysis is effected by heating the neat material at 160 °C for 6 h in the presence of a catalytic amount of stainless steel. The complex decomposition leads to 3,3-dimethyl-1-(methylthio)-2-butanone oxime, *N,N'*-dimethylurea, carbon dioxide, pivalonitrile, methylthioacetonitrile, and several other products. The proposed mechanism for the first few steps of the decomposition includes a dissociation of 3,3-dimethyl-1-(methylthio)-2-butanone oxime and methyl isocyanate, a metal-catalyzed formation to 3,3-dimethyl-1-(methylthio)-2-butanone *O*-(*N,N'*-dimethylallophanoyl)oxime (**19**), and subsequent thermal decomposition of **19**. Evidence is given to support the proposed first few steps of the decomposition.

O-[(Methylamino)carbonyl]ald and ketoximes constitute a class of important carbamate insecticides. Well-known examples include aldicarb [2-methyl-2-(methylthio)-propanal *O*-[(methylamino)carbonyl]oxime (**1**)], 2,4-di-



methyl-2-[carboxaldehyde-*O*-[(methylamino)carbonyl]-oxime]-1,3-dithiolane (**2**), and thiofanox [3,3-dimethyl-1-(methylthio)-2-butanone *O*-[(methylamino)carbonyl]-oxime (**3**)]. The thermal reactions of this class of compounds have received some attention in the literature. For example, the thermal decomposition of aldicarb in benzene solution is reported to produce 2-methyl-2-(methylthio)-propionitrile (**5**), carbon dioxide, and methylamine [eq 1



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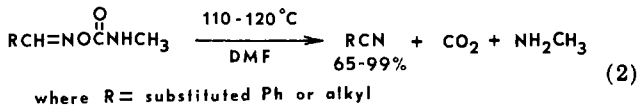
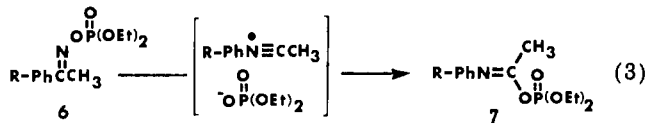


where R = substituted Ph or alkyl

(2)

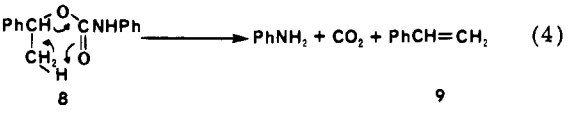
(Payne et al., 1966)]. The decomposition of *O*-[(methylamino)carbonyl]aldoximes in dimethylformamide was shown to decompose in a similar fashion [eq 2 (Albright and Alexander, 1972)]. Bellet and Fukuto reported the thermal rearrangement of substituted acetophenone *O*-(diethylphosphoryl)oximes (**6**) to imidoyl phosphates (**7**) [eq 3 (Bellet and Fukuto, 1972)]. Thus, *O*-[(methyl-



(3)

amino)carbonyl]aldoximes appear to decompose by an intramolecular cyclic mechanism to produce nitriles, carbon dioxide, and methylamine, whereas the mode of decomposition of the *O*-(diethylphosphoryl)oximes appear to follow a thermal Beckmann rearrangement.

The mode of decomposition of the aldoximes is very similar to that observed in a related class of compounds, i.e., *O*-alkyl *N*-phenylcarbamates. However, the decomposition of α-methylbenzyl *N*-phenylcarbamate (**8**) produced styrene (**9**) instead of a nitrile [eq 4 (Dyer and



(4)

Wright, 1959)]. For other modes of thermal decomposition of *O*-alkyl *N*-arylcarbamates, see Dyer and Read (1961).

In our experience with oxime carbamates, particularly the insecticide thiofanox (**3**), inconsistent but significant differences in thermal stability were observed between pure and impure samples. We would like to report that certain metals cause thiofanox to decompose. In order to obtain additional information about the stability of impure samples, we initiated a study of the fundamental chemistry transpiring during the decomposition. We now report our findings on the nonsolution thermal chemistry of thiofanox (**3**).

MATERIALS AND METHODS

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Perkin-Elmer R24B spectrometer by using Me_4Si as an internal standard unless stated otherwise. Natural-abundance ^{13}C NMR spectra were obtained at 22.53 MHz with complete proton decoupling on a Bruker WH-90 spectrometer. All samples were dissolved in $CDCl_3$ for field-frequency locking, and chemical shifts were referenced to Me_4Si. Infrared spectra (IR) were recorded on a Perkin-Elmer Model 137 infrared spectrophotometer. All boiling points and melting points are reported uncorrected. Gas chromatography was carried

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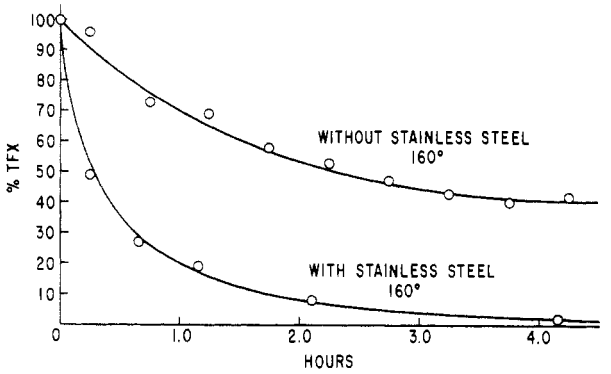


Figure 1. Effect of stainless steel on the thermal decomposition of thiofanox (TFX).

out on a Varian 3700 (FID) gas chromatograph by using the CDS 111 data system. The temperature program used was as follows: started with a column temperature of 32 °C for 5 min, then heated at a rate of 8 °C/min to 150 °C, and maintained at 150 °C for 35 min. The column used was an 8-ft stainless steel column packed with 20% SP 2100 plus 1% Carbowax on 100/120 Supelcoport. A Varian CH7 mass spectrometer interfaced with a Varian 1740 gas chromatograph was used in the GC–MS phase of this study. All EI mass spectra were recorded at 70 eV.

Metal-Catalyzed Pyrolysis of Thiofanox (3). To a 250-mL three-necked round-bottomed flask fitted with a mechanical stirrer, thermometer, and condenser was added 50.0 g (0.229 mol) of pure (*Z*)-thiofanox (recrystallized from CH_2Cl_2–heptane) and 0.10 g of stainless steel (No. 316). The reaction flask was immersed in an oil bath preheated to 160 °C. Half-gram aliquots were taken periodically for quantitative analysis. After 4.13 h the pyrolysis was terminated, and a red-brown oil resulted. During the decomposition a white solid accumulated on the condenser. At the end of the reaction, the solid was isolated and stored in a capped serum bottle. A Tygon tubing connection from the condenser exit of the reaction flask to a wet test meter allowed the measurement of the amount of gases given off. Other catalysts that were found to effect the thermal decomposition were lead, iron, and lead naphthenate.

Isolation and Characterization of the Thermal Decomposition Products. The isolation of the decomposition products was simplified by dividing the unknown products into three general groups based on volatility. The gases and volatile constituents at room temperature constituted the first group of products, i.e., headspace samples. They were separated and analyzed by GC–MS. The volatile products that could be trapped in a liquid nitrogen trap after subjecting the complex mixture to low pressure (10^{-3} torr) made up the second group. These were also analyzed by GC–MS. The third group was composed of the higher boiling unknowns that could not be readily vaporized. This group was subjected to preparative medium-pressure chromatography (silica gel/gradient elution) and fractional vacuum distillation. A complete list of all of the products identified are tabulated in Table I. The spectral data (^{1}H NMR, ^{13}C NMR, IR, and MS) on each product has been tabulated and can be found in the supplemental material of this paper (see paragraph at end of paper regarding supplementary material). The white solid that was collected was identified as ammonium carbamate by IR.

Quantitative Analyses of the Products. Because of the diverse range of properties of the products, it was necessary to use two gas chromatographs to achieve a complete analysis. The amount of carbon dioxide was determined on a Fisher-Hamilton gas partitioner with a

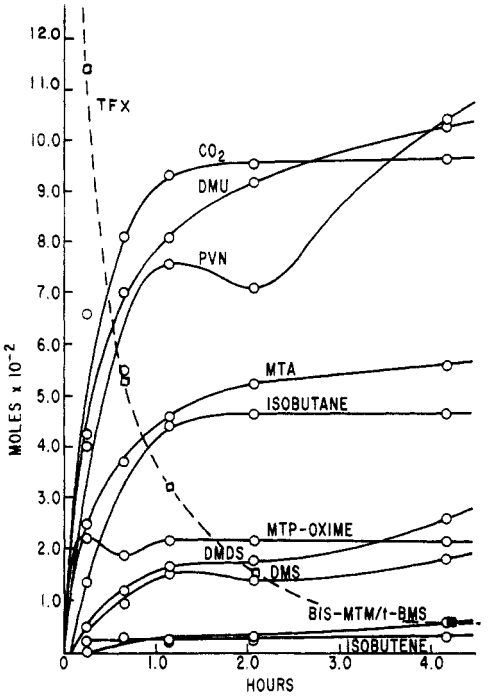


Figure 2. Concentration of products of decomposition vs. time.

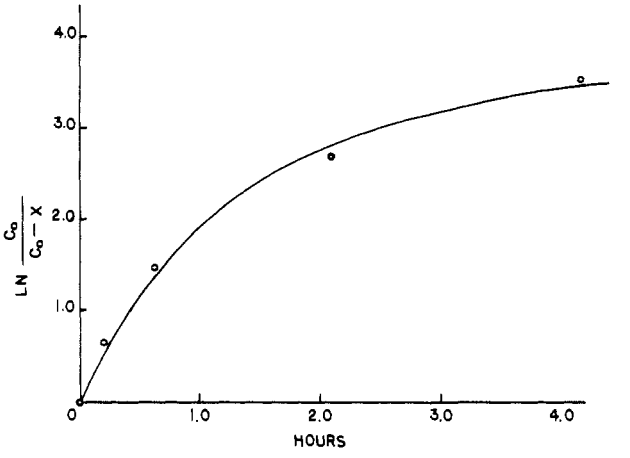


Figure 3. First-order plot for the disappearance of thiofanox.

6 ft × $^{13}/_{16}$ in. column filled with molecular sieves (40–60 mesh; 13X). The gaseous organics were analyzed in a Perkin-Elmer 910 gas chromatograph with a 10 ft × $^1/_8$ in. glass column containing 20% SP 2100 plus 1% Carbowax on 100/120 Supelcoport. The liquid samples were analyzed on a Varian HA 300-MHz ^{1}H NMR spectrometer. Quantitative analysis was performed on dimethyl disulfide. All other measurements were then related to this value by proton integration. The estimated accuracy was ±5%. The disappearance of thiofanox vs. time is plotted in Figure 1. The molar amounts of the major products vs. time is plotted in Figure 2. Components that were present in trace quantities were not included in the quantitation. The observed spectrum of products account for about 71% of the decomposed thiofanox at each analysis point. The appropriate kinetic plots for the disappearance of thiofanox were made: i.e., first order, ln $[c_0/(c_0 - x)]$ vs. hours (Figure 3); second order, $[x/[c_0 - x)]]$ vs. hours (Figure 4); three-halves order, $2(c^{-1/2} - c_0^{-1/2})$ vs. hours (Figure 5).

Pyrolysis of Thiofanox (3). The same procedure described above was used with the exception that the catalyst was left out. The ^{1}H NMR spectrum and gas chromatographic analysis of the pyrolysate were identical with those obtained during the catalyzed decomposition. The dis-

Table I. Pyrolysis Products of Thiofanox (3) and Allophanate (19)

ammonia
ammonium carbamate
bis(methylthio)methane (BMTM)
tert-butyl alcohol
tert-butyl methyl sulfide (*tert*-BMS)
N-*tert*-butyl-2-(methylthio)acetamide (16)[b]
N-*tert*-butyl-*N'*-methylurea[b]
carbon dioxide
carbon monoxide
carbon oxysulfide[a]
dimethyl cyanurate
3,3-dimethyl-1,1-bis(methylthio)-2-butanone
N,N'-dimethyl-*N*-(methylaminocarbonyl)urea (14)
3,3-dimethyl-1-(methylthio)-2-butanone *O*-*tert*-butyloxime (13)
3,3-dimethyl-1-(methylthio)-2-butanone *O*-(*N,N'*-dimethylallophanoyl)oxime (19)
1,2-bis(methylthio)ethane[a]
3,3-dimethyl-1-(methylthio)-2-butanone *O*-[(methylthio)carbonyl]oxime (18)[b]
3,3-dimethyl-1-(methylthio)-2-butanone *O*-(methylthiomethyl)oxime (11)
3,3-dimethyl-1-(methylthio)-2-butanone oxime (10) (MTP-oxime)[c]
dimethyl sulfide (DMS)
dimethyl sulfone
N,N'-dimethylurea (DMU)
isobutane
isobutylene
methyl isocyanate
(methylthio)acetonitrile (21) (MTA)
(methylthio)pinacolone (MTP)
pinacolone
pivalonitrile (20) (PVN)

[a] Found in the thiofanox decomposition only. [b] Found in the allophanate (19) decomposition only. [c] MTP-oxime is a product of the thiofanox decomposition but was added to the decomposition of 19.

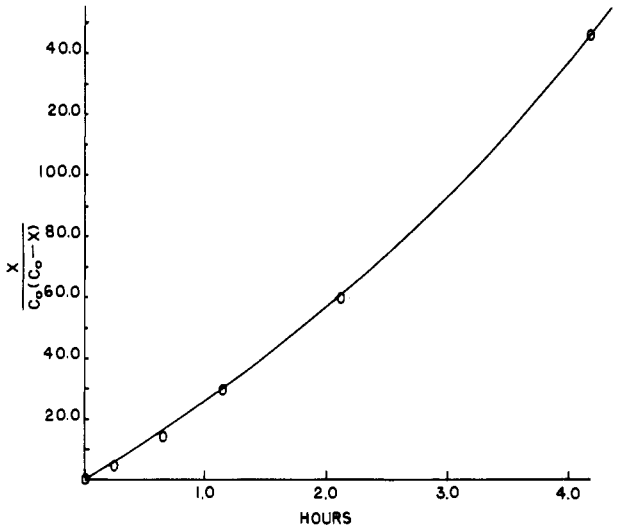


Figure 4. Second-order plot for the disappearance of thiofanox.

appearance of thiofanox vs. time is plotted in Figure 1.

Preparation of *tert*-Butyl Methyl Sulfide. To 4.0 g (0.10 mol) of NaOH in 75 mL of H_2O was added 11.3 mL (0.10 mol) of *tert*-butyl mercaptan. To the resulting solution was added 6.2 mL (0.10 mol) of methyl iodide and a few milligrams of hexadecyltri-*n*-butylphosphonium bromide. The two-phased system was heated at 60 °C for 1 h and cooled, and the organic layer was separated. The aqueous layer was extracted with an equal volume of diethyl ether. The combined extract and organic oil were dried (Na_2SO_4) and concentrated by rotary evaporation to give 0.48 g (4.6%) of crude oil. The low yield resulted from losses due to volatilization. Spectral data (IR, MS, and ^1H NMR) were consistent with the desired sulfide (see supplementary material).

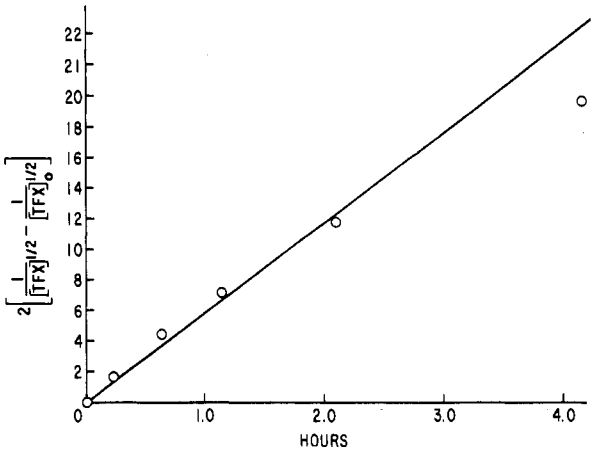


Figure 5. Three-halves-order plot for the disappearance of thiofanox.

Preparation of *N,N'*-Dimethyl-*N*-[(methylamino)carbonyl]urea (14). To 0.526 g (5.97×10^{-3} mol) of *N,N'*-dimethylurea was added 4 mL of methyl isocyanate. After the mixture was allowed to stand at room temperature for 60 h, long white needles precipitated from the solution. The crystals were collected by vacuum filtration, washed with diethyl ether, and air-dried. A total of 0.487 g (56%) of 14 was obtained as white needles, mp 124–126 °C. The ^1H NMR and IR spectra were consistent with said structure.

(*O*-*tert*-Butylhydroxyl)amine Hydrochloride. This material was prepared by reacting sodium *tert*-butoxide with chloramine (Coleman and Johnson, 1939) according to the procedure of Thielacker and Ebke (1956). The compound was a white crystalline solid (mp 155–156 °C). A major byproduct was hydroxylamine hydrochloride.

3,3-Dimethyl-1-(methylthio)-2-butanone *O*-*tert*-Butyloxime (13). A mixture of 4.75 g (0.033 mol) of (methylthio)pinacolone (freshly distilled), 5.46 g (0.0455 mol) of (*O*-*tert*-butylhydroxyl)amine hydrochloride, 48 mL of ethanol (absolute), and 29 mL of pyridine was refluxed 24 h. After concentration to half volume by rotary evaporation, the solution was poured into an equal volume of saturated ammonium chloride solution and was extracted with three portions of diethyl ether. The ether extracts were washed with H_2O, two portions of 5% HCl, and H_2O. Drying ($MgSO_4$) and concentrating gave 6.11 g (87%) of a yellow oil. Preparative medium-pressure chromatography (silica gel/ether–hexane (1:1) at 6 mL/min) gave 5.04 g (71%) of the *O*-*tert*-butyl derivative as a colorless oil. All spectral data (IR, ^1H NMR, ^{13}C NMR, and MS) as well as elemental analysis support the said structure.

3,3-Dimethyl-1-(methylthio)-2-butanone *O*-(Methylthio)methyloxime (11). In a dry inert atmosphere 14.6 g (0.0981 mol) of (methylthio)pinacolone oxime was added slowly to a stirring slurry of 2.86 g (0.119 mol) of sodium hydride in 200 mL of dimethyl sulfoxide (previously distilled from CaH_2). After the evolution of gas ceases (2 h), chloromethyl methyl sulfide (9.7 g, 0.10 mol) was added slowly over 25 min. After being stirred at room temperature for 1.5 h, the reaction mixture was poured onto 600 mL of ice. The aqueous phase was extracted with an equal volume of diethyl ether. The ether extract was washed with 3 × 15 mL of water and dried ($MgSO_4$). Concentration by rotary evaporation gave 19.45 g of an amber oil (87% pure by GC; XE-60 column). Fractional vacuum distillation gave 11.2 g of 11.

***N*-*tert*-Butyl-2-(methylthio)acetamide (16).** To a solution of methanethiol (0.25 g, 0.0052 mol) in 1 mL of dimethylformamide stirring at 0 °C under nitrogen was added *N*-*tert*-butyl-2-chloroacetamide (0.375 g, 0.0025 mol), potassium carbonate (0.414 g, 0.003 mol), and 4 mL of DMF. The mixture was stirred at room temperature for 18 h. The reaction mixture was poured into water and extracted with ether. The ether layer was washed with 5% NaOH, 5% HCl, H_2O, and saturated NaCl solution. Drying ($MgSO_4$) and concentrating gave ca. 0.3 g of **16** as a white crystal mp 41–43 °C. This was sublimed at 32 °C (0.02 mm) to yield 0.28 g.

3,3-Dimethyl-1-(methylthio)-2-butanone *O*-[(Methylthio)carbonyl]oxime (18). A solution of 3,3-dimethyl-1-(methylthio)-2-butanone *O*-(chlorocarbonyl)-oxime (**17**) (1.90 g, 0.0085 mol) in 40 mL of anhydrous ether was cooled to 0 °C and added in one portion to 1.00 g (0.0208 mol) of methanethiol, with stirring, at −70 °C. An 0.80-g (0.0080-mol) sample of triethylamine was added. The mixture was allowed to warm to 25 °C. The precipitate was removed by filtration. The filtrate was concentrated to give 1.5 g of clear light yellow oil (75% yield). The IR, ^1H NMR, and MS were consistent with the expected structure. The (methylthio)carbonyl derivative (**18**) was thermally unstable and degraded very slowly while stored at 0 °C.

Preparation of the 3,3-Dimethyl-1-(methylthio)-2-butanone *O*-(*N*,*N*′-Dimethylallophanoyl)oxime (19). A solution of 16.1 g (0.100 mol) of 3,3-dimethyl-1-(methylthio)-2-butanone oxime (**10**) in 100 mL of anhydrous ether was added in one portion to a solution of 12.3 g (0.125 mol) of phosgene (phosgene dissolved in benzene can be used) in 200 mL of ether, with stirring, at −70 °C. After being stirred for 16 h at room temperature, the clear colorless solution was concentrated by rotary evaporation to give a clear colorless oil consisting of *O*-chlorocarbonyl oxime (**17**) (97%). (**Caution**: Large quantities of this material have been found to decompose vigorously at room temperature with the evolution of gaseous products.) The oil was immediately diluted with 500 mL of ether and was cooled to −70 °C. Finely powdered *N*,*N*′-dimethylurea (11.0 g, 0.125 mol) was added. The mixture was stirred and allowed to come to room temperature over a 60-h period. The ethereal solution was washed with water, dried (Na_2SO_4), and concentrated by rotary evaporation to yield 25.7 g of yellow oil. The ^1H NMR spectrum of this crude product indicated that it was 60% **19**. The major impurity was bis[3,3-dimethyl-1-(methylthio)-2-butanone] *O*,*O*′-carbonyldioxime as indicated by TLC (silica gel; 25% ether–hexane; UV). Medium-pressure preparative liquid chromatography gave 11.1 g (54%) of high-purity allophanate as a white solid, mp 43 °C. The spectral data (IR, ^1H NMR, ^{13}C NMR, and MS) and elemental analysis was consistent with the expected structure (see supplementary material).

Deuterium-Labeled Thiofanox. The synthesis of 3,3-dimethyl-1-(methylthio)-1,1-dideuterio-2-butanone *O*-[(methylamino)carbonyl]oxime (thiofanox-d_2) and 3,3-dimethyl-1-(methylthio)-2-butanone *O*-[(trideuteriomethylamino)carbonyl]oxime (thiofanox-d_3) have been described (Corkins et al., 1980b). The ^1H NMR spectrum of thiofanox-d_2 indicated 88% deuterium labeling at the C-1 position. The ^1H NMR spectrum of thiofanox-d_3 indicated 99% deuterium at the *N*-methyl carbon. A thiofanox-d_2–thiofanox-d_3 mixture was prepared by grinding in a mortar and pestle 2.0092 g of thiofanox-d_3 and 2.000 g of thiofanox-d_2. This mixture was used in the crossover experiments. The EI mass spectrum of the thiofanox-d_2–thiofanox-d_3 mixture was obtained. The isotopic distribution observed for the parent ion region of this sample is summarized in Table II. For additional details of the fragmentation of thiofanox, see Corkins et al. (1980b).

Table II. EI Mass Spectrum of Thiofanox (3): Isotopic Distribution for the Parent Ion Region[a]

	d_0	d_1	d_2	d_3	d_4	d_5
thiofanox-d_2,d_3 mixture	0	21	61	100	25	6
mixture after isolation by chromatography	7	17	63	100	25	12
placed under reaction conditions and reisolated	93	41	88	100	52	69

[a] d_0 represents thiofanox containing no deuterium, M_r 218; d_1, M_r 219; d_2, M_r 220; d_3, M_r 221; d_4, M_r 222; d_5, M_r 223.

As a check on any possible exchange occurring during the isolation of thiofanox, a 0.2738-g sample of the thiofanox-d_2-thiofanox-d_3 mixture was subjected to preparative thick-layer chromatography (silica gel/70:30 ether–hexane). Reisolation gave 0.2718 g which was subjected to mass spectral analysis. The isotopic distribution observed for the parent ion region of the recovered sample is shown in Table II.

Pyrolysis of the Thiofanox-d_2–Thiofanox-d_3 Mixture. The pyrolysis of the thiofanox-d_2–thiofanox-d_3 mixture was carried out under the identical conditions described for the metal-catalyzed decomposition. The decomposition was stopped after 15 min which represented about 50% decomposition. Undecomposed deuterium-labeled thiofanox was reisolated by thick-layer chromatography and subjected to mass spectral analysis. The isotopic distribution observed for the parent ion region of the reisolated sample is reported in Table II.

Metal-Catalyzed Addition of Methyl Isocyanate to Thiofanox (3). The following general procedure was used to determine the affect of catalyst on the reaction between thiofanox and methyl isocyanate. A single-necked 100-mL round-bottomed flask was charged with 2.0 g (0.0092 mol) of thiofanox, 2.0 mL (1.93 g, 0.034 mol) of freshly distilled methyl isocyanate, catalyst, and 20 mL of methylene chloride. The catalysts and the amounts used were as follows: lead naphthenate (100 mg), powdered iron (2.0 g), lead (100 mg), and stainless steel (100 mg). The reaction mixture was refluxed for 72 h and subjected to HPLC analysis (C_8 reverse phase; 25 × 0.4 cm; H_2O–MeOH). The reaction of thiofanox with methyl isocyanate to produce allophanate (**19**) was determined by comparison of retention times of the products from the reaction mixture with that of authentic **19**. In the lead naphthenate catalyzed run, **19** was the major product (100% yield) and was obtained after 8 h. In the stainless steel catalyzed reaction, the HPLC peak that corresponded to **19** was isolated and determined unequivocally to be **19** by ^1H NMR. Thermal decomposition of thiofanox was observed in all of the catalyzed reactions except for the lead naphthenate case. The relative amounts of decomposition were not determined.

Pyrolysis of 3,3-Dimethyl-1-(methylthio)-2-butanone *O*-(*N*,*N*′-Dimethylallophanoyl)oxime (19). To a 100-mL three-necked round-bottomed flash fitted with magnetic stirrer, thermometer, and condenser was added 4.00 g (0.0145 mol) of **19**, 2.34 g (0.0145 mol) of 3,3-dimethyl-1-(methylthio)-2-butanone oxime (**10**), and 0.100 g of stainless steel. The flask was immersed in an oil bath preheated to 160 °C. The thermal decomposition was

terminated after 6 h. The pyrolysate was cooled to room temperature. A total of 1.6 g had been lost in the form of gas or volatile material. The gases and volatile components were analyzed by GC–MS. The volatile compounds that could be trapped in a liquid nitrogen trap after subjecting the pyrolysate to low pressure (10^{-3} torr) were also analyzed by GC–MS. The nonvolatile residue (3.9 g) was stirred in 30 mL of ether, and the insoluble solid was removed by filtration. The solid (0.46 g) consisted of 0.32 g of *N,N'*-dimethylurea (separated by dissolving in hot ethyl acetate). The filtrate was rotary evaporated to yield 3.16 g of red-brown oil. The oil was subjected to medium-pressure liquid chromatography (EM silica gel; particle size 43–60 μm; 3 × 40 cm column; step gradient elution; flow rate 4 mL/min). The various components of the chromatography fractions as well as the volatile liquids were characterized by ^{1}H NMR, GC, GC–MS, IR, and TLC. A complete list of the compounds isolated from the decomposition of **19** is given in Table I.

RESULTS AND DISCUSSION

(*Z*)-Thiofanox (**3**) was thermally decomposed at 160 °C without the influence of solvent. The decomposition occurred rapidly and was accompanied by a gradual darkening of the colorless melt. There was evidence of gas evolution. In the uncatalyzed reactions, the rate of decomposition was rapid at first but after about 4 h became sluggish at approximately 50% completion (Figure 1). The addition of metals, e.g., stainless steel, iron, lead, or lead naphthenate, accelerated the decomposition. The use of stainless steel catalyst caused almost complete decomposition after 4 h. Except for the obvious difference in the relative amounts of thiofanox, the ^{1}H NMR spectra of the pyrolysates of both the catalyzed and uncatalyzed decompositions were essentially identical.

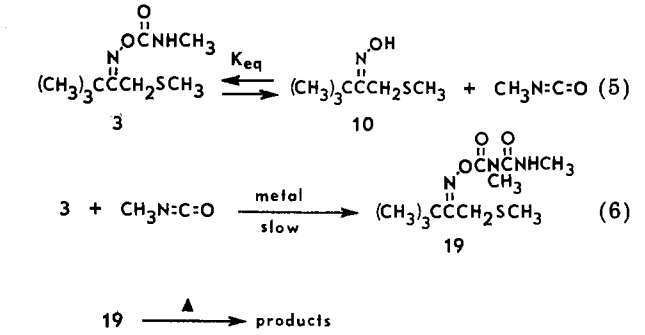
Thiofanox (**3**) thermally decomposes to a complex mixture of products. The products were isolated by a variety of standard techniques. Identification of most of the products was made by spectral comparisons to authentic samples that were either prepared independently or reported in the literature. Many of the minor and trace products were identified by their mass spectra obtained by gas chromatography–mass spectral analysis. A complete list of the isolated products can be found in Table I.

From the products isolated and their structural variety, it was clear that several additional thermal reactions of the initially formed products had taken place. Direct evidence for these reactions was obtained by adiabatic calorimetry experiments. However, these experiments and these secondary decompositions were beyond the scope of this study. The decomposition of the ketoxime **3** was not as clean as those reported for aldoximes or, for that matter, the *O*-alkyl phenylcarbamates.

For establishment of the initial modes of thiofanox decomposition attention was focused at finding out which of the isolated products were formed first. Thus, the course of the decomposition was monitored with time. The relative amounts of the products formed vs. time were determined, and these data are summarized in Figure 2. A total of 78% of decomposed thiofanox was accounted for as the products shown in Figure 2.

A study of Figure 2 leads to several conclusions about the thermal reaction. First, 3,3-dimethyl-1-(methylthio)-2-butanone oxime (**10**), carbon dioxide, *N,N'*-dimethylurea, pivalonitrile (**20**), isobutane, and methylthioacetonitrile (**21**) are among the first formed products. Second, several of the first formed products are undergoing further decomposition, e.g., **10** and pivalonitrile. Third, the formation of 1 mol of carbon dioxide and 1 mol of

Scheme I

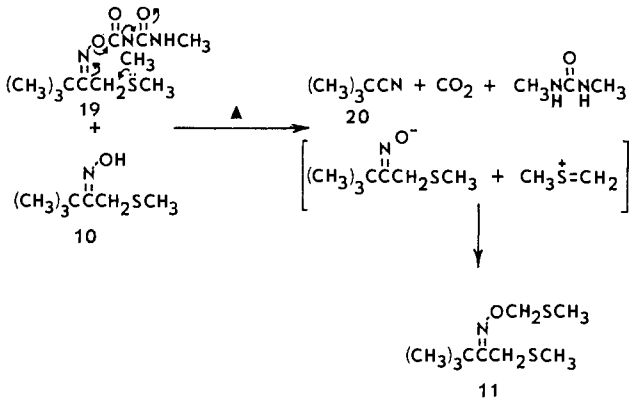


N,N'-dimethylurea requires the decomposition of 2 mol of thiofanox. Fourth, several of the observed products appear to be produced by secondary thermal reactions, e.g., isobutane, dimethyl disulfide, and dimethyl sulfide. And finally, the concentration of many of the minor isolated products do not appear to build up during the course of the reaction. The last point is particularly important and not unexpected since many of the minor products isolated are structurally similar to the thiofanox and would not survive the reaction conditions. The products listed in Table I that are not noted in Figure 2 were not formed in sufficient quantities, i.e., <1%.

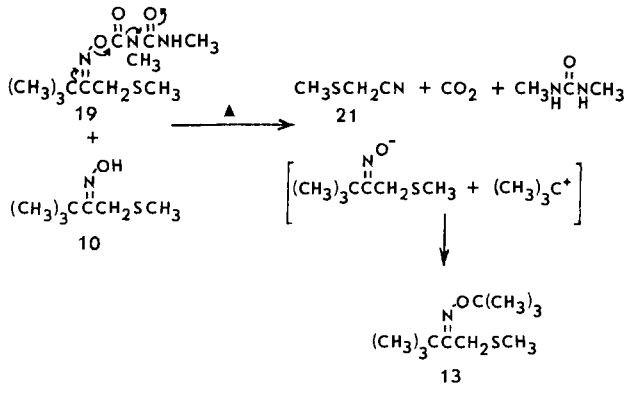
A kinetic analysis with respect to the disappearance of thiofanox was carried out. Appropriate plots for a first, second, and three-halves-order reaction were prepared (Figures 3, 4, and 5, respectively). The reaction was determined not to be first order as shown by the lack of linearity of the plot ln $[c_0/(c_0 - x)]$ vs. time (Figure 3). Thus, a unimolecular rate determining homolytic or heterolytic cleavage of the nitrogen–oxygen bond does not appear to be operating. This mode of decomposition has been reported (Dyer and Wright, 1959). The structures **11** and **13** would also argue against such a process. Unfortunately, the actual order of the reaction cannot be determined by the data. As can be seen by Figures 4 and 5, reasonable straight lines were obtained from the second- and three-halves-order plots. These results arise from the inaccuracies of the analytical methods, i.e., ^{1}H NMR for determining the concentration of thiofanox. Attempts at improving the data were unsuccessful. Kinetic analysis of the pressure rise accompanying the decomposition suggested, however, the order of the reaction to be three-halves. But the multitude of products contributing to the gases make this result tenuous. The only firm conclusion that could be reached is that the reaction is definitely not first order but is of higher order, i.e., second or three-halves. A second- or three-halves-order reaction would be consistent with the observation that 2 mol of thiofanox must decompose to give 1 mol of carbon dioxide.

After consideration of several possible explanations to account for the first formed products, the proposed sequence of reactions shown by Scheme I was favored. The first step involves reversible dissociation of the thiofanox molecule to methyl isocyanate and 3,3-dimethyl-1-(methylthio)-2-butanone oxime (**10**) (eq 5). This dissociation has precedent from the work of Dyer and Wright, who reported this mode of decomposition exclusively for *O*-ethyl *N*-phenylcarbamate (Dyer and Wright, 1959). The second step of the sequence is the addition of methyl isocyanate to a second molecule of thiofanox, producing **19** (eq 6). Evidence for this reaction comes from the isolation of **19** from the reaction mixture and studies on the metal-catalyzed addition of methyl isocyanate to thiofanox to be described. The third step proposed involves the thermal decomposition of the allophanate **19** by two possible

Scheme II



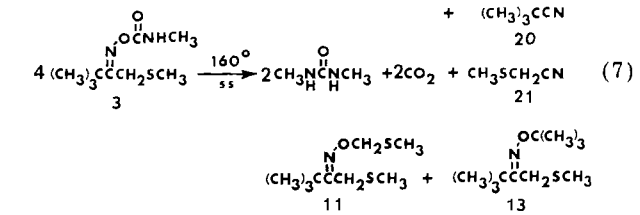
Scheme III



thermal Beckmann rearrangements (Schemes II and III) similar to that observed by Bellet and Fukuto (1972).

The decomposition shown in Scheme II would result in pivalonitrile (**20**), carbon dioxide, *N,N'*-dimethylurea, methylthiomethyl cation, and (methylthio)pinacolone oxime anion. Reaction of the anion and cation would reasonably explain the formation of **11**. The alternate route for the decomposition of **19** in the presence of **10** is shown in Scheme III. (Methylthio)acetonitrile (**21**), carbon dioxide, *N,N'*-dimethylurea, *tert*-butyl cation, and (methylthio)pinacolone oxime anion would be the immediate products. Again, the combination of the ions would reasonably explain the formation of **13**.

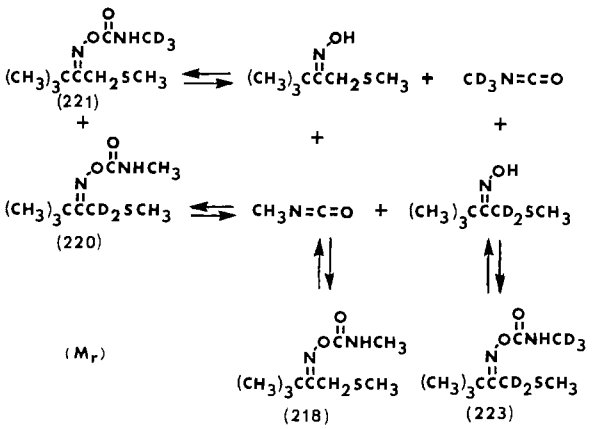
The overall stoichiometry for the processes as written in Schemes I–III is given by eq 7. All of the observed first



(7)

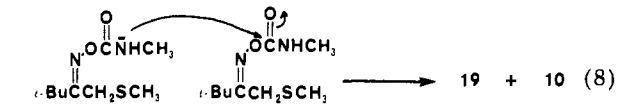
formed products, i.e., *N,N'*-dimethylurea, carbon dioxide, pivalonitrile (**20**), and (methylthio)acetonitrile (**21**), are accounted for. Notice the expected amounts of *N,N'*-dimethylurea and carbon dioxide require twice the amount of thiofanox (**3**) to decompose as was observed (see Figure 2). The relative amounts of pivalonitrile (**20**) and (methylthio)acetonitrile (**21**) would be expected to reflect the relative rates of the alternate decomposition pathways available to **19** as well as reflect their stability under the reaction conditions. The higher concentration of **20** suggests the route shown by scheme II is favored. This result supports the concept of an unstable intermediate since

Scheme IV



direct decomposition of thiofanox (**3**) by a thermal Beckmann rearrangement would be expected to favor the formation of (methylthio)acetonitrile (**21**) (Corkins et al., 1980a). The small amounts of **11** and **13** isolated as well as the larger amounts of 3,3-dimethyl-1-(methylthio)-2-butanone oxime (**10**) suggest that other degrative reactions are available to the anions and cations produced and/or that **11** and **13** are unstable under the reaction conditions.

The proposed mechanism would be consistent with a three-halves-order reaction if the second step was rate limiting. Alternatively, a bimolecular reaction of **3** with itself to produce **19** and **10** cannot be ruled out (eq 8). The



(8)

result of the bimolecular reaction would be the same as that depicted in eq 7.

For establishment of the reversibility of the first step as described by eq 5, a crossover experiment using deuterium-labeled thiofanox was carried out. The experiment involved making an equimolar mixture of thiofanox-d_2 and thiofanox-d_3. The thiofanox-d_2 had the deuterium label α to the imine carbon–nitrogen double bond. The thiofanox-d_3 had the deuterium label on the *N*-methyl substituent of the molecule. After subjecting the mixture to the reaction conditions, undecomposed thiofanox was recovered and subjected to mass spectral analysis. If a reversible dissociation was occurring, thiofanox-d_0 and thiofanox-d_5 should be detected. Scheme IV indicates the origin of the new compounds. The results of the crossover experiments are summarized in Table II. The large increase in the thiofanox-d_0 and thiofanox-d_5 species relative to the control indicated the reversible dissociation of **3** to methyl isocyanate and **10** was indeed taking place under the reaction conditions. Less than 10% of the dissociation resulted from chromatographic workup. Also, the dissociation was found to occur in the presence or absence of metal catalysts after heating at 150–160 °C for 1 h, whereas less than 10% dissociation occurred in methylene chloride solution at 25 °C after 3 h. A reversible thermal dissociation of methyl isocyanate from *O*-aryl *N*-methylcarbamates has been reported (Dyer and Wright, 1959; Krishna et al., 1962).

Focusing now on understanding the second step of the mechanism proposed in Scheme I, the metal-catalyzed addition of methyl isocyanate to thiofanox (**3**) to produce the allophanate (**19**) was studied. This reaction was demonstrated to occur most readily in the presence of metals. For example, the addition of a large excess of methyl isocyanate to thiofanox did not produce **19** under mildly

forcing conditions, i.e., refluxing methyl isocyanate. However, the addition of a catalytic amount of lead naphthenate to a refluxing methylene chloride solution of methyl isocyanate and **3** facilitated the addition quantitatively (eq 9). The use of iron, lead, or stainless steel in

$$\text{N. R.} \xleftarrow{CH_3NCO} 3 \xrightarrow[Pb^{++}]{CH_3NCO} 19 \qquad (9)$$

the reaction catalyzed the production of **19** but to a much lesser extent. The difference in efficiencies could be attributed to the heterogeneousness of the latter catalysts. Thus, the possibility of the action described by eq 6 has been demonstrated. Since the difference between the catalyzed and uncatalyzed reactions is relative rates, it must be assumed that at 150 °C the addition of methyl isocyanate to **3** can occur in the absence of metals.

As a test of step 3 of the proposed mechanism (Scheme I), the allophanate (**19**) was prepared independently and subjected to the thermal reaction conditions. **19** was decomposed in the presence of an equivalent amount of 3,3-dimethyl-1-(methylthio)-2-butanone oxime (**10**) and 0.02% (by weight) stainless steel. The products of the decomposition were found to be identical with those obtained from the decomposition of **3**. The products are listed in Table I. The several additional trace components reported for the allophanate reflect an increased ability to isolate and identify these materials rather than a difference in the reactions. There was no trace of thiofanox (**3**) in the pyrolysate, indicating **19** had not reverted back to **3** which then decomposed. The decomposition of **19** was faster than loss of methyl isocyanate.

In summary, the thermal decomposition of thiofanox (**3**) has been studied. Although the reaction is complicated by several secondary decompositions of the initially formed products, a reaction sequence for the critical first few steps was proposed. Direct and indirect evidence for the proposed mechanism includes the deuterium-labeled crossover experiment, indicating the dissociation of thiofanox to **10** and methyl isocyanate, independent synthesis and thermal decomposition of **19** to give the same products as thermally decomposed **3**, the stoichiometric relationship of **3** to *N,N'*-dimethylurea and carbon dioxide, the independent demonstration of the metal-catalyzed addition of methyl isocyanate to thiofanox, the isolation of **19** from decomposed thiofanox, and the observation of higher order kinetics. Although we favor the sequence in Scheme I, the bimolecular reaction of **3** as in eq 8 cannot be ruled out.

From this study it is clear that the mode of thermal decomposition of the ketoxime carbamate, thiofanox, is more complex than that reported for the decomposition of aldoxime carbamates. The metal catalysis is a new complex feature of the thermal chemistry that has not been noted in previous investigations. We suggest the principles outlined here can be applicable to other oxime carbamates that are placed in an environment of moderately elevated temperature and contact with metals and/or metal salts, e.g., during manufacture or in the soil.

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Supplementary Material Available: Analytical and spectral data (6 pages). Ordering information is given on any current masthead page.

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