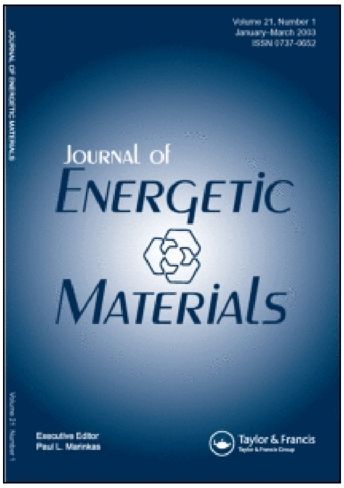


Journal of Energetic Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

Relative rates of CH_3NO_2, CH_3ONO, and CH_3ONO_2 formation in the thermal reaction of NO_2 with acetaldehyde and DI-T-butyl peroxide at low temperatures

S. C. Cooper[ab]; M. E. Umstead[a]; E. Kolby[a]; M. C. Lin[a]
[a] Naval Research Laboratory, Chemistry Division, Washington, D.C. [b] Department of Chemistry, Cornell University, Ithaca, N.Y.

To cite this Article Cooper, S. C. , Umstead, M. E. , Kolby, E. and Lin, M. C.(1989) 'Relative rates of CH_3NO_2, CH_3ONO, and CH_3ONO_2 formation in the thermal reaction of NO_2 with acetaldehyde and DI-T-butyl peroxide at low temperatures', Journal of Energetic Materials, 7: 1, 55 — 76
To link to this Article: DOI: 10.1080/07370658908012560
URL: http://dx.doi.org/10.1080/07370658908012560

RELATIVE RATES OF CH_3NO_2, CH_3ONO, AND CH_3ONO_2 FORMATION IN THE THERMAL REACTION OF NO_2 WITH ACETALDEHYDE AND DI-T-BUTYL PEROXIDE AT LOW TEMPERATURES

S. C. Cooper[a], the late M. E. Umstead, E. Kolby[b], and M. C. Lin

Chemistry Division
Code 6105
Naval Research Laboratory
Washington, D.C. 20375-5000

ABSTRACT

The relative yields of CH_3NO_2, CH_3ONO, and CH_3ONO_2 have been measured at five temperatures between 323 and 455 K above 300 torr of pressure. Kinetic modelling of the observed $CH_3NO_2/(CH_3ONO + CH_3ONO_2)$ and CH_3ONO/CH_3ONO_2 ratios from this study and that of Phillips and Shaw (Ref. 5), with and without added NO, led to the rate constant for $CH_3 + NO_2 \longrightarrow CH_3NO_2$ (1), $k_1 = 6.0 \times 10^{12}$ cc/mol-sec, and for $CH_3O + NO_2 \longrightarrow CH_3ONO_2$ (4), $k_4 = 7.5 \times 10^{12}$ cc/mol-sec. The results of the modelling also indicate that the oxidation of CH_3NO by NO_2 accounts for a large fraction of CH_3NO_2 formed in the NO-added mixtures. The rate constant for this reaction is estimated to be $k_{25} \cong 1.3 \times 10^9 e^{(-10,000/RT)}$ cc/mol-sec. Combination of k_1 with the equilibrium constant for reaction (1) gives rise to the rate constant for the decomposition of CH_3NO_2, $k_{-1} = 1.3 \times 10^{16} e^{(-60,050/RT)}$ sec^{-1}.

---

a. Summer student, Department of Chemistry, Cornell University, Ithaca, N.Y. 14853.
b. DoD Science and Engineering Apprentice (1986-87).

INTRODUCTION

The reaction of the CH_3 radical with NO_2 is the principle chain propagation step in the CH_3NO_2 thermal decomposition reaction[1], which has been frequently employed as a model energetic material system. The CH_3 + NO_2 reaction can occur via two distinctly different intermediates, nitromethane and methyl nitrite:

$$
\begin{aligned}
CH_3 + NO_2 \longrightarrow CH_3\text{-}NO_2^{\dagger} &\longrightarrow CH_3NO_2 && (1)\\
\longrightarrow CH_3\text{-}ONO^{\dagger} &\longrightarrow CH_3ONO && (2a)\\
&\longrightarrow CH_3O + NO && (2b)\\
&\longrightarrow CH_2O + HNO, && (2c)
\end{aligned}
$$

where "$\dagger$" represents a vibrationally excited reaction intermediate. For the channel occurring via $CH_3ONO^{\dagger}$, the production of the methoxy radical, CH_3O, has been shown to be dominant, and the stabilization step (a) and the four-centered HNO elimination process, step (c), have been shown to be unimportant over broad ranges of temperatures and pressures[2].

The absolute rate constant for CH_3NO_2 formation, k_1, has not been reliably measured[3]. The best measurements reported in the literature were based on the product ratio $CH_3NO_2/(CH_3ONO + CH_3ONO_2)$, which gives rise to the relative rate constant, k_1/k_2. The CH_3ONO and CH_3ONO_2 products result mainly from the recombination reactions of the CH_3O radical with NO and NO_2 present in the system:

$$
\begin{aligned}
CH_3O + NO &\longrightarrow CH_3ONO && (3)\\
CH_3O + NO_2 &\longrightarrow CH_3ONO_2. && (4)
\end{aligned}
$$

Thus, under excess NO_x conditions, the total rate of CH_3ONO_x formation should provide a reliable estimate for the total rate of reaction (2), $CH_3 + NO_2 \longrightarrow CH_3O + NO$.

The value of k_1/k_2 has been reported by several authors. Rebbert and Slagg[4] first presented a value of $k_1/k_2 = 0.42$ at 298 K in the photodissociation of CH_3NO_2 in the presence of NO. In a more extensive study by Phillips and Shaw[5], who pyrolyzed mixtures of NO_2, CH_3CHO, and neopentane (as a buffer gas) with or without added NO, three rate constant ratios, $k_1/k_2 = 0.50$, $k_3/k_4 = 1.8$, and $k_2/k_5 = 0.30$, were obtained at 363 K. Here, k_5 is the rate constant for the recombination reaction,

$$CH_3 + NO \longrightarrow CH_3NO. \qquad (5)$$

In a similar study of the thermal reaction of NO_2 with C_2H_4 (which was postulated as occurring via the vibrationally excited CH_3CHO molecule), Chao and Jaffe[6] reported the ratio of $k_1/k_2 = 0.36$ at 298 K, which is in close agreement with the values given above. Accordingly, the value of the rate constant ratio, k_1/k_2, appears to be fairly reliably determined. This value, combined with the absolute rate constant recently derived for k_2 covering a broad range of experimental conditions, should provide a reliable estimate for k_1.

The absolute value for k_2 has been measured recently by Gutman and co-workers to be $(1.51 \pm 0.30) \times 10^{13}$ cc/mol-sec at room temperature using the method of laser photoinitiation and photoionization mass spectrometry[7]. This value is in close agreement with that reported by Glanzer and Troe, $k_2 = 1.33 \times 10^{13}$ cc/mol-sec from their study of CH_3NO_2 decomposition in the temperature range 1200-1400 K under highly diluted conditions[8]. These results have been recently corroborated by our shock tube - CO laser resonance absorption data carried out in the 950-1200 K temperature range[2]. The RRKM-theoretical analysis of these three sets of data covering the 300-1400 K temperature range leads to the expression[2],

$$k_2 = 7.7 \times 10^{10} T^{0.64} e^{980/RT} \text{ cc/mol-sec.}$$

This equation was employed in our detailed kinetic modelling of the experimental data of Phillips and Shaw[5] and of the results obtained in the present study.

In this study, we have employed different mixtures of both acetaldehyde and di-t-butyl peroxide with NO_2, with and without added NO, covering a broader range of temperatures than has been used before. The relative yields of CH_3NO_2, CH_3ONO, and CH_3ONO_2 were accurately measured by gas chromatography under varying experimental conditions. The measured product ratios were kinetically modelled with a computer.

EXPERIMENTAL

Commercial acetaldehyde (Aldrich) and di-t-butyl peroxide (MCB) were stored as liquids after purification by trap-to-trap distillation. Both were employed as sources of the CH_3 radical at low temperatures. Nitrogen dioxide (Matheson) was purified by thorough pumping at dry ice temperature to remove traces of nitric oxide. Nitric oxide (Matheson) was purified by passing through a silica gel trap maintained at dry ice temperature to remove nitrogen dioxide. Argon (Matheson, 99.999% pure) was used without further purification.

Mixtures of acetaldehyde or di-t-butyl peroxide, nitric oxide, nitrogen dioxide, and argon were prepared in a one liter bulb and allowed to stand at room temperature for one hour or longer before experiments. Analysis showed that no reaction occurred at room temperature, even when the mixtures were allowed to stand overnight. In preparing the mixtures, a correction was made for nitrogen dioxide concentration to account for the presence of N_2O_4 at room temperature. The experiments were carried out at 343, 363, and 383 K for the acetaldehyde mixtures and at 445 and 455 K for the di-t-butyl peroxide mixtures for a set time in a stirred, temperature-controlled oil bath. The reaction was quenched by removing the bulb from the oil bath and quickly cooling it with tap water. The concentrations of nitromethane, methyl nitrite, methyl nitrate, and acetaldehyde (or di-t-butyl peroxide) in the bulb were measured by passing a ten-torr sample of the product gas through a Beckman GC-5 gas chromatograph with a six foot long, quarter inch stainless steel column containing polyethylene glycol 400. The resultant peaks were quantified with a Hewlett Packard 3990A integrator.

Nitromethane, methyl nitrite, and methyl nitrate were all required for calibrations. Nitromethane (Fisher) was distilled and collected at 374-375 K. It was further purified by freezing and pumping. Methyl nitrite was prepared by adding sulfuric acid to sodium nitrite in a methanol-water solution.[9] Methyl nitrate was synthesized, as described by Black and Babers[10], by adding sulfuric acid and nitric acid to methanol diluted in dibutyl phthalate. Both samples were purified by trap-to-trap distillation prior to use.

RESULTS AND DISCUSSION

The ratios of the yields of nitromethane, methyl nitrite, and methyl nitrate obtained from typical sets of experiments are shown in Figures 1 and 2, respectively, with and without added nitric oxide. Since the amount of sample introduced into the gc varied slightly between runs, only the relative quantities of the products were measured. Relative product measurement also provides more reproducible results. Typically, the ratios $CH_3NO_2/(CH_3ONO + CH_3ONO_2)$ and CH_3ONO/CH_3ONO_2, to be denoted by NM/(MI + MA) and MI/MA throughout the text, were found to increase with reaction time, approaching some limiting values after about one hour of pyrolysis.

The product ratios presented in Figures 1 and 2 clearly show the effect of added NO. In the absence of NO (Figure 2), the NM/(MI + MA) remains essentially unchanged with the length of reaction time. With the addition of NO to the reaction mixture, as indicated by the results shown in Figure 1, both product ratios, MI/MA and NM/(MI + MA), vary noticeably with reaction time. Additionally, the NM/(MI + MA) ratio was markedly increased by added NO. A similar pronounced enhancement in the NM/(MI + MA) yield ratio was noted when the total pressure of an NO-added reaction mixture was increased, as shown by the result in Figure 3. Additional data taken from different mixtures and reaction conditions are summarized in Table I, together with the kinetically modelled results. A detailed discussion on kinetic modelling is given below.

Kinetic Modelling

The variation of the product ratios with time and NO concentration, as described above, cannot be understood and quantified without a detailed kinetic simulation using a realistic reaction mechanism. To achieve these goals, we have set up a reasonable reaction scheme, as listed in Table II, to simulate the observed product ratios under different experimental conditions. The reaction mechanism was based partly on that derived by Phillips and Shaw[5] and partly on our previously established mechanisms for CH_3NO_2[1] and $(CH_3)_2NNO_2$[11] decomposition reactions. We have recently reported that the CH_3NO_2 product formed in the thermal decomposition of $(CH_3)_2NNO_2$ at low temperatures derives exclusively from reaction (1)[11].

In the present system, the initiation process is the direct bimolecular reaction of NO_2 with acetaldehyde by C-H abstraction[5,12]:

$$CH_3CHO + NO_2 \longrightarrow CH_3CO + HONO. \qquad (6)$$

The CH_3 radical can be generated by the known unimolecular and bimolecular processes:

$$CH_3CO \longrightarrow CH_3 + CO \qquad (7)$$

$$CH_3CO + NO_2 \longrightarrow CH_3 + CO_2 + NO. \qquad (8)$$

The rate constant for these CH_3-production reactions can be found in the literature[3,13].

The initiation process in the di-t-butyl peroxide + NO_2 system can be quantitatively described by the well established reactions[13]:

$$(t\text{-}C_4H_9)_2O_2 \longrightarrow 2t\text{-}C_4H_9O \qquad (6')$$

$$t\text{-}C_4H_9O \longrightarrow CH_3 + CH_3COCH_3 \qquad (7')$$

The rate constants for these reactions in the high-pressure region are also available in the literature[13]. It should be pointed out that, for the purpose of modelling the product ratios MI/MA and NM/(MI + MA), the accuracy of these CH_3-radical initiation processes is unimportant, as substantiated by the result of our brief sensitivity test.

The subsequent processes following the reactions of interest:

$$CH_3 + NO_2 \longrightarrow CH_3NO_2 \qquad (1)$$

$$\longrightarrow CH_3O + NO, \qquad (2)$$

are listed in Table II, together with the "best" available rate constants. The result of the sensitivity analysis indicates that, under the high-pressure ($p \geq 100$ torr), low temperature conditions employed in the present work and in Phillips and Shaw's experiments, only reactions (1) - (5) and (25) are important for the description of the relative rates of CH_3NO_2, CH_3ONO, and CH_3ONO_2 production. Other processes which strongly affect the absolute yields of these products are included for a more realistic simulation. The inclusion of the less important CH_3O + NO_x disproportionation reactions:

$$CH_3O + NO \longrightarrow CH_2O + HNO \qquad (6)$$

$$CH_3O + NO_2 \longrightarrow CH_2O + HONO \qquad (7)$$

(which were neglected in Phillips and Shaw's steady-state treatment) causes a slight change in the modelled k_1/k_2 ratio because these reactions account for the lost CH_3O which is not converted into CH_3ONO_x.

All of the experimentally measured MI/MA and NM/(MI + MA) data, including those of Phillips and Shaw[5], were kinetically modelled. The computer profiles of these product ratios as functions of time for mixture I ($CH_3CHO:NO:NO_2:Ar$ = 36:71:98:360) are shown in Figure 1; the solid curves were obtained for these two ratios with $k_{25} = 1.1 \times 10^3$ cc/mol-sec, and the dotted line for the NM/(MI + MA) ratio with $k_{25} = 0$. The exclusion of reaction (25) has essentially no effect on the computed MI/MA ratio. The computed results shown in Figure 2 for NM/(MI + MA) taken from experiments using mixture G with no added NO indicate that the effect of reaction (25) is negligible as expected. The observed values also remain constant as theoretically predicted. The importance of reaction (25) in the presence of NO is again demonstrated by the results presented in Figure 3 where the total pressure of NO-added mixtures is varied. The observed experimental data could not be accounted for without including reaction (25), as indicated by the result represented by the dotted line. By comparing all the data collected from experiments with and without added NO, we are able to arrive at a reasonable value for k_{25} at different temperatures.

The modelled rate constants and some of their ratios are summarized in Tables I and III. By taking $k_2=7.7\times10^{10}T^{0.64}e^{(980/RT)}$ and $k_3=6.0\times10^{12}$ cc/mol-sec, the rate constant ratios given in Table I give rise to

$$k_1=(6.0\pm0.1)\times10^{12} \text{ cc/mol-sec}$$

and

$$k_4=(7.5\pm2.3)\times10^{12} \text{ cc/mol-sec.}$$

An Arrhenius analysis of the values of k_{25} leads to the following approximate expression:

$$k_{25}\cong1.3\times10^9e^{(-10,000/RT)} \text{ cc/mol-sec.}$$

It is worthwhile to compare these rate constants with other relevant measurements. By steady-state treatment, Phillips and Shaw[5] arrived at the rate constant ratios $k_1/k_2=0.46$ from the $CH_3CHO + NO_2$ reaction at 363 K under high pressure conditions and $k_1/k_2=0.50$ and $k_5/k_2=0.30$ from the pyrolysis of the CH_3CHO-NO_2 mixtures in the presence of varying amounts of NO, also at 363 K using more than 100 torr of total pressure. Taking the value of k_2 adopted in Table II, the above rate constant ratios lead to

$$k_1=(6.3\pm0.2)\times10^{12} \text{ cc/mol-sec}$$

and $$k_5=3.3\times10^{12} \text{ cc/mol-sec.}$$

The former value is in excellent agreement with our kinetically modelled value, 6.0×10^{12} cc/mol-sec, and the latter is in good accord with the value obtained by Basco et al., 2.4×10^{12} cc/mol-sec[15] as given in Table II. The k_1/k_2 ratio obtained at 298 K by Rebbert and Slagg[4], $k_1/k_2=0.42$ gives rise to $k_1=6.3\times10^{12}$ cc/mol-sec and that of Chao and Jaffe[6], $k_1/k_2=0.36$, to $k_1=5.4\times10^{12}$ cc/mol-sec. These values are all in much closer agreement with the present result than that obtained indirectly by Lloyd et al., 2.4×10^{12} cc/mol-sec, from the pyrolysis of dimethylnitramine at 472-524 K under high pressure conditions[11].

The combination of the present result, $k_1=(6.0\pm0.1)\times10^{12}$ cc/mol-sec, with the equilibrium constant for $CH_3NO_2 = CH_3 + NO_2$, $K_{-1}=2.14\times10^{3}e^{(-60,050/RT)}$ mol/cc leads to the rate constant for the unimolecular decomposition of CH_3NO_2:

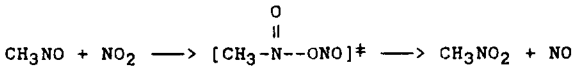
$$k_{-1}=1.3\times10^{16}e^{(-60,050/RT)} \text{ sec}^{-1}.$$

This result compares very nicely with the extrapolated high-pressure rate constant by Glanzer and Troe[8]:

$$k_{-1}=1.8\text{x}10^{16}e^{(-59,000/RT)}\ \text{sec}^{-1}.$$

Since the MI/MA ratio depends strongly on the amounts of NO and NO_2 present in the system, the values of k_3/k_4 obtained from computer modelling appear to be more scattered. Sensitivity analysis also showed its dependence on tertiary processes such as reactions (26)-(28). To test the validity of k_3/k_4 ratios from the present modelling, we also attempted to simulate the observed MI/MA as a function of initial NO/NO_2 ratios as presented in Figure 4. The values for MI/MA agree closely with the experimental values. It should be pointed out that, although the slope of the MI/MA - NO/NO_2 plot, as indicated in the figure, is as high as 1.92, the rate constant ratio, k_3/k_4 is only about 0.8. Thus, we cannot equate the slope of this plot to the k_3/k_4 ratio, at least not for the present case.

Finally, it is also worthwhile to address the nature of reaction (25), which accounts, to a large extent, for the CH_3NO_2 produced in the presence of NO. This reaction is believed to be due to the direct oxidation:



$$CH_3NO + NO_2 \longrightarrow [CH_3\text{-}\overset{\overset{O}{\|}}{N}\text{--}ONO]^{\ddagger} \longrightarrow CH_3NO_2 + NO$$

rather than the exchange mechanism. At low temperatures, CH_3NO is known to exist in dimer forms with a dissociation energy of about 23 kcal/mol[13]. (The N atom in CH_3NO is thus expected to be reactive.) The rate constant obtained for reaction (25) appears to be reasonable for such an NO_2 oxidation process.

CONCLUSION

Kinetic modelling of the relative product yields of CH_3NO_2, CH_3ONO, and CH_3ONO_2 produced in the thermal reaction of NO_2 with acetaldehyde and t-butyl peroxide in the temperature range 323-455 K, measured under high pressure conditions in the present study and partly in the study by Phillips and Shaw[5], leads to the value of the rate constant for $CH_3 + NO_2 \longrightarrow CH_3NO_2$: $k_1 = (6.0 \pm 0.1) \times 10^{12}$ cc/mol-sec; $CH_3O + NO_2 \longrightarrow CH_3ONO_2$: $k_4 = (7.5 \pm 2.3) \times 10^{12}$ cc/mol-sec and $CH_3NO + NO_2 \longrightarrow CH_3NO_2 + NO$: $k_{25} \cong 1.3 \times 10^9 e^{(-10,000/RT)}$ cc/mol-sec. Combination of k_1 with the equilibrium constant for reaction (1) gives rise to the rate constant for the decomposition of CH_3NO_2, $k_{-1} = 1.3 \times 10^{16} e^{(-60,050/RT)}$ sec^{-1}.

Table I

Experimental and Modelled Results[a]

Mixture	T/K	P/torr	CH_3ONO/CH_3ONO_2		k_3/k_4	$CH_3NO_2/(CH_3ONO+CH_3ONO_2)$		k_1/k_2
			expt	model		expt	model	
A[b]	363	630	1.42	1.41	0.70	0.86	0.83	0.46
B	363	524	1.84	1.80	0.94	0.83	0.81	0.46
C	363	313	0.99	1.00	0.48	0.75	0.78	0.46
D	363	577	0.93	0.96	0.89	0.75	0.71	0.46
E	363	576	0.66	0.63	0.70	0.72	0.67	0.46
F	363	640	0.26	0.24	0.80	0.56	0.55	0.46
G	363	611	0	0.02	-	0.48	0.47	0.47
H	363	555	-	-	-	1.5	1.2	0.46
I	383	565	1.92	1.86	0.94	0.86	0.86	0.46
J	343	565	0.92	0.95	0.46	0.76	0.78	0.46
K[c]	445	558	-	-	-	0.79	0.79	0.48
L	455	558	-	-	-	0.77	0.76	0.50

(a) Data presented are for one hour of pyrolysis at 363 and 383 K, two hours of pyrolysis at 343 K, and 30 min of pyrolysis at 445 and 455 K.

(b) The reagent ratios for mixtures A-J given as acetaldehyde:nitric oxide:nitrogen dioxide:argon are: Mixture A: 40:80:110:400; Mixture B: 33:66:91:334; Mixture C: 20:40:53:200; Mixture D: 36:47:125:369; Mixture E: 34:40:133:369; Mixture F: 38:8.5:211:382; Mixture G: 7:0:202:402; Mixture H: 7:102:43:402; Mixture I: 36:71:98:360; Mixture J: 36:71:98:360.

(c) The reagent ratios for mixtures K and L given as di-t-butyl peroxide:nitric oxide:nitrogen dioxide:argon are: Mixture K: 14:38:42:464; Mixture L: 14:38:42:464.

Table II

Reactions and Rate Constants Used in Modelling the Low-Temperature Reaction of Acetaldehyde or di-t-butyl peroxide With NO_2[a]

Reaction	A	B	E_a	Ref.
(1) CH_3 + NO_2 ---> CH_3NO_2	6.0 E12	0	0	this work
(2) CH_3 + NO_2 ---> CH_3O + NO	7.7 E10	0.64	0.98	2
(3) CH_3O + NO ---> CH_3ONO	6.0 E12[b]	0	0	14
(4) CH_3O + NO_2 ---> CH_3ONO_2	7.5 E12	0	0	this work
(5) CH_3 + NO ---> CH_3NO	2.4 E12	0	0	15
(6) CH_3CHO + NO_2 ---> CH_3CO + HONO	2.5 E10	0	12.4	3
(7) CH_3CO ---> CH_3 + CO	2.0 E10	0	15	13
(8) CH_3CO + NO_2 ---> CH_3 + CO_2 + NO	1.0 E12	0	0	16
(6') $(t\text{-}C_4H_9)_2O_2$ ---> $2t\text{-}C_4H_9O$	6.3 E15	0	37.8	13
(7') $t\text{-}C_4H_9O$ ---> CH_3 + CH_3COCH_3	3.2 E13	0	8.25	13
(9) CH_3O + NO ---> CH_2O + HNO	1.2 E13	0	2.3	14[b]
(10) CH_3O + NO_2 ---> CH_2O + HONO	5.8 E12	0	2.3	17
(11) CH_3CO + HNO ---> CH_3CHO + NO	1.0 E12	0	0	c
(12) CH_3ONO ---> CH_3O + NO	4.0 E15	0	41.1	13
(13) CH_3ONO_2 ---> CH_3O + NO_2	3.2 E15	0	39.5	13
(14) CH_3NO + 2NO ---> CH_3 + N_2 + NO_3	2.6 E06	0	-1.8	18
(15) NO_3 + NO ---> $2NO_2$	4.2 E12	0	1.71	3
(16) NO_3 + NO_2 ---> NO_2 + O_2 + NO	1.4 E11	0	3.18	3
(17) CH_3O + CH_3CHO ---> CH_3OH + CH_3CO	1.0 E11	0	3.0	c

Table II

Reactions and Rate Constants Used in Modelling the Low-Temperature Reaction of Acetaldehyde With NO_2[a] (continued)

Reaction	A	B	E_a	Ref.
(18) $CH_3 + CH_3CHO \longrightarrow CH_4 + CH_3CO$	8.5 E10	0	6.0	3
(19) $CH_3O + CH_2O \longrightarrow CH_3OH + HCO$	1.0 E11	0	3.0	19
(20) $CH_3 + CH_2O \longrightarrow CH_4 + HCO$	1.1 E11	0	6.1	3
(21) $HCO + NO \longrightarrow CO + HNO$	7.2 E13	-0.4	0	20
(22) $HCO + NO_2 \longrightarrow CO + HONO$	1.6 E13	0	-0.43	21
(23) $CH_3 + HNO \longrightarrow CH_4 + NO$	5.0 E11	0.5	0	22
(24) $CH_3O + HNO \longrightarrow CH_3OH + NO$	3.2 E13	0	0	14
(25) $CH_3NO + NO_2 \longrightarrow CH_3NO_2 + NO$	1.3 E09	0	10	this work
(26) $HNO + HNO \longrightarrow N_2O + H_2O$	8.5 E08	-	3.1	14
(27) $HNO + HONO \longrightarrow H_2O + 2NO$	8.5 E08	-	3.1	c
(28) $HONO + HONO \longrightarrow H_2O + NO + NO_2$	8.5 E08	-	3.1	c

(a) Rate constants, in the form $k = AT^B \exp(-E_a/RT)$, are in cc/mol-sec, and E_a, kcal/mol.
(b) Pressure dependent; the value given is for 550 torr Ar.
(c) Assumed.

Table III

Rate Constants Obtained from Kinetic Modelling[a]

Mixture[b]	T/K	P/torr	$k_1/10^{12}$	$k_4/10^{12}$	$k_{25}{}^c/10^3$	Ref.
A	363	630	6.0	8.6	1.5	d
B	363	524	6.0	6.3	1.2	d
C	363	313	6.0	10.5	0.9	d
D	363	577	6.0	6.8	1.5	d
E	363	576	6.0	8.6	2.1	d
F	363	640	6.0	8.0	1.4	d
I	383	565	6.0	6.4	1.2	d
J	343	565	6.0	11.0	1.0	d
K	445	558	6.2	3.8	20	d
L	455	558	6.5	3.4	20	d
M	363	340	6.0	8.0	1.6	e
N	363	567	6.0	8.0	1.6	e
O	363	305	5.5	-	-	e
P	363	411	5.7	-	-	e
Q	363	492	5.7	-	-	e
G	363	610	6.1	-	-	d
R	328	410	5.9	-	-	e
Average			6.0±0.1	7.5±2.3		

(a) The rate constants are in units of cc/mol-sec.

(b) The reagent ratios for mixtures A-G and I-L listed in Table I. Reagent ratios for mixtures M-R given as acetaldehyde:nitric oxide:nitrogen dioxide:neopentane are: Mixture M: 24:36:42:238; Mixture N: 24:35:41:467; Mixture O: 8:0:200:97; Mixture P: 8:0:200:203; Mixture Q: 8:0:200:284; Mixture R: 8:0:200:202.

(c) These data lead to $k_{25} \cong 1.3\text{x}10^9\exp(-10{,}000/RT)$.

(d) This work

(e) Results obtained by kinetic modelling of the data of Phillips and Shaw (ref. 5).

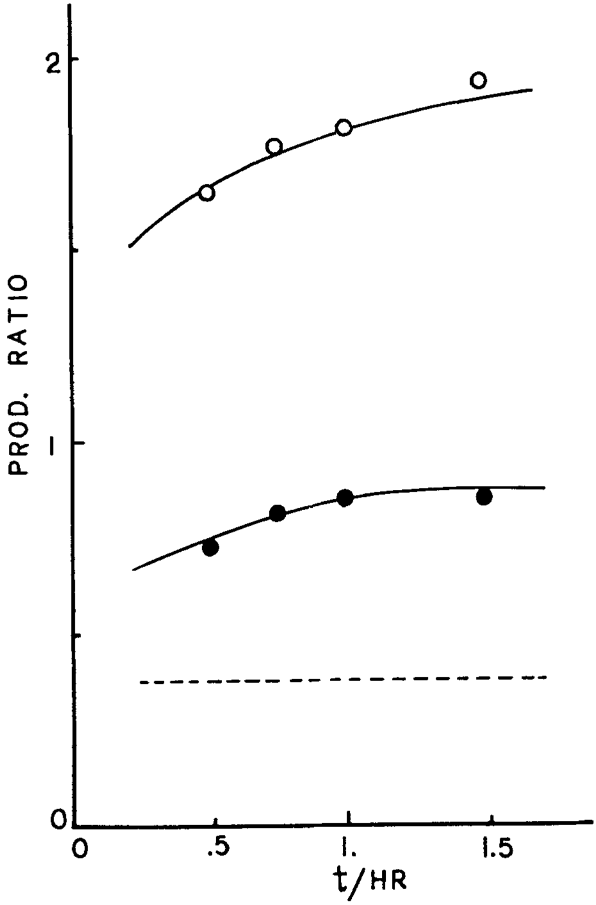


FIGURE 1

Relative product yields, CH_3ONO/CH_3ONO_2 (open circles) and $CH_3NO_2/(CH_3ONO + CH_3ONO_2)$ (filled circles) measured at 363 K as functions of reaction time using mixture A (see Table I for composition and total pressure). Solid curves: calculated values based on the mechanism given in Table II including reaction (25); dotted line: the same calculation for the $CH_3NO_2/(CH_3ONO + CH_3ONO_2)$ ratio without reaction (25). Reaction (25) has no effect on the CH_3ONO/CH_3ONO_2 ratio.

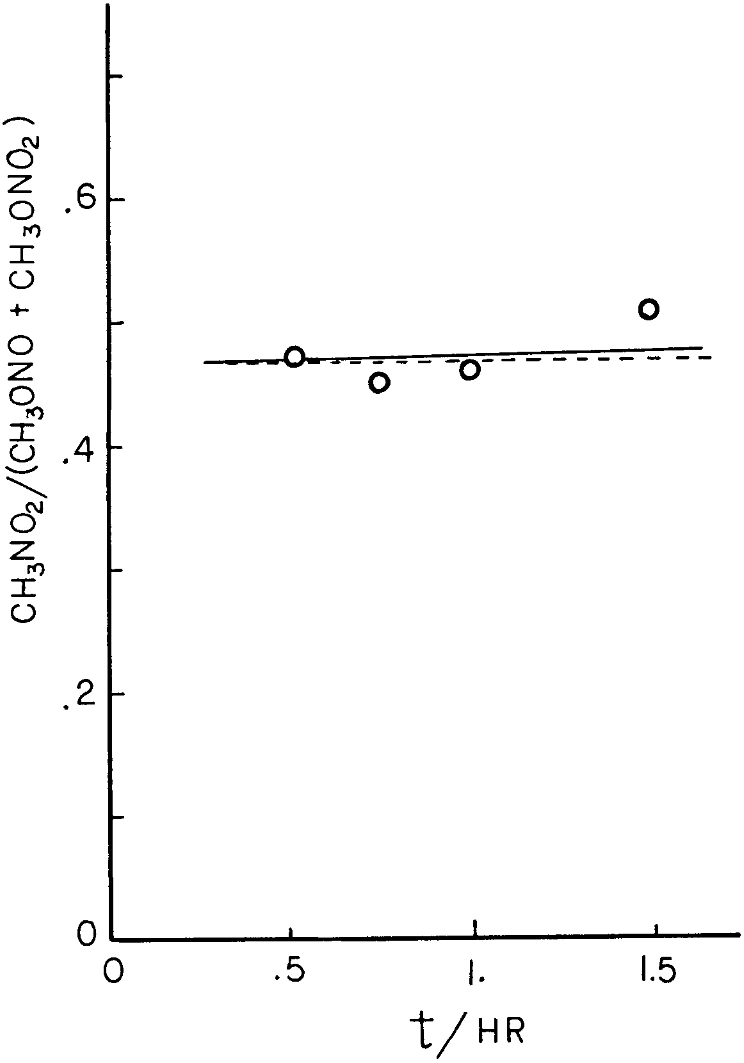


FIGURE 2

The $CH_3NO_2/(CH_3ONO + CH_3ONO_2)$ ratio as a function of time using reaction mixture G (see Table I for composition and total pressure) at 363 K without added NO. Solid and dotted lines: calculated values with and without reaction (25).

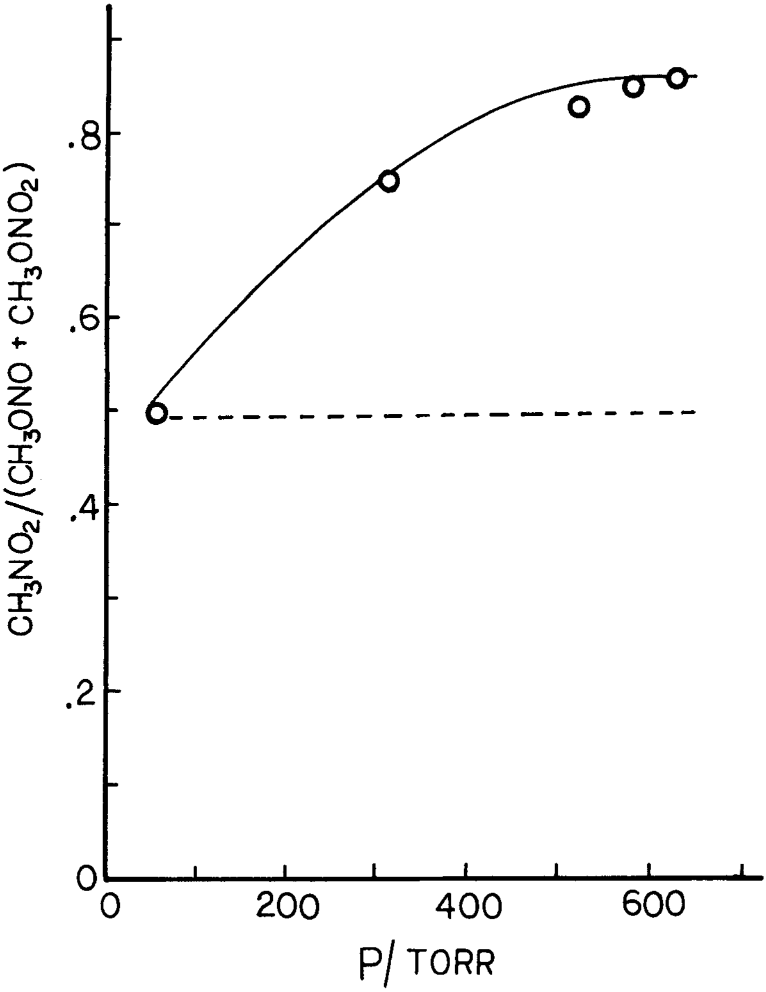


FIGURE 3

The $CH_3NO_2/(CH_3ONO + CH_3ONO_2)$ ratio as a function of reaction pressure measured at 363 K after one hour of reaction using mixtures A-C (which have the compositions as given in Table I). Solid and dotted curves: calculated values, with and without reaction (25).

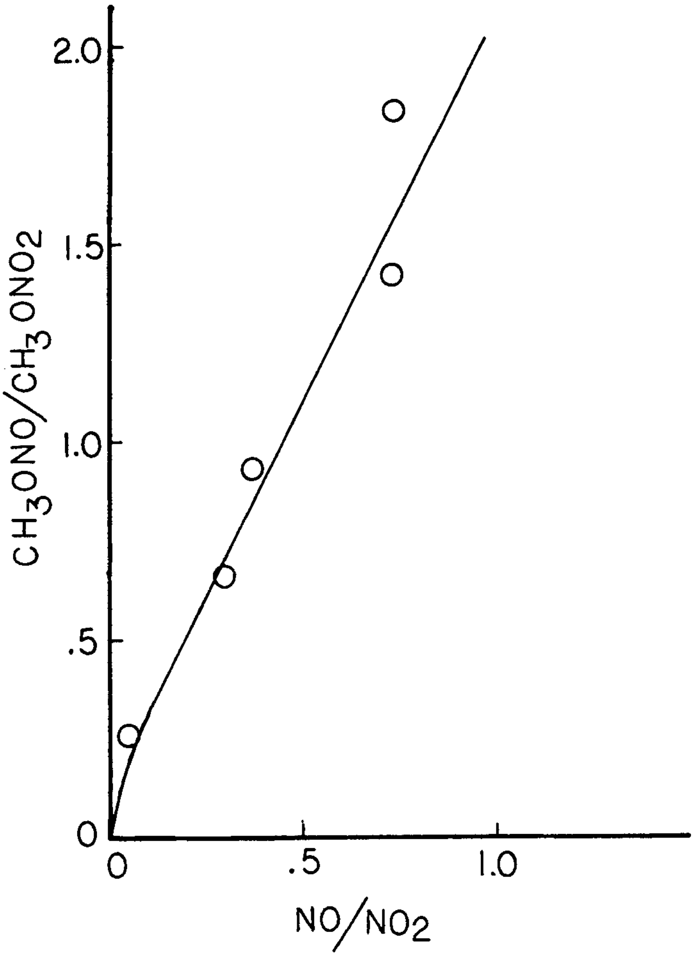


FIGURE 4

The dependence of the CH_3ONO/CH_3ONO_2 ratio on the relative concentration of NO and NO_2 at 363 K using runs A, B, C, D, E, F, and G as given in Table I. The solid curve represents the modelled values using $k_4=7.8\times10^{12}$ cc/mol-sec.

REFERENCES

1. D.S.Y. Hsu and M.C. Lin, J. Energ. Mat. 3, 95(1985).

2. S.C. Cooper, C.Y. Lin, A. Argetsinger and M.C. Lin, 1986 Fall Technical Meeting, Eastern Section of the Combustion Institute,(Extended abstract, p. 29-1), Dec. 15-17, 1986, San Juan, Puerto Rico.

3. J.A. Kerr and S.J. Moss, Handbook of Bimolecular and Termolecular Gas Reactions, vol. 1 CRC Press, 1981.

4. R.E. Rebbert and N. Slagg, Bull. Soc. Chim. Belges 71, 709(1962).

5. L. Phillips and R. Shaw, 10th Symp. (Int.) on Combustion, p. 453, The Combustion Institute, 1965.

6. S.C. Chao and S. Jaffe, J. Chem. Phys. 56, 1987(1972).

7. F. Yamata, I. Slagle and D. Gutman, Chem. Phys. Lett. 83, 409(1981).

8. K. Glanzer and J. Troe, Helv. Chim. Acta 55, 2884(1972).

9. W. Theilheimer, Syn. Methods of Org. Chem. 16, 415(1966).

10. A.P. Black and F.H. Babers, Org. Syn. 2, 412(1943).

11. S.A. Lloyd, M.E. Umstead and M.C. Lin, J. Energ. Mat. 3, 187(1985).

12. A.E. Pedler and F.H. Pollard, Trans. Faraday Soc. 53, 44(1957).

13. S.W. Benson and H.E. O'Neal, Kinetic Data on Gas Phase Unimolecular Reactions, NSRDS-NBS 21, National Bureau of Standards, 1970.

14. Y. He, W.A. Sanders and M.C. Lin, J. Phys. Chem., in press.

15. N. Basco, D.G.L. James and R.D. Suart, Int. J. Chem. Kinet. 2, 215(1970).

16. M.I. Christie and M.A. Voisey, Trans. Faraday Soc. 63, 2702(1967).

17. J.M. Caulley, S.M. Anderson, J.B. Jeffries and F. Kaufman, Chem. Phys. Lett. 115, 180(1985).

18. M.I. Christie, J.S. Frost and M.A. Voisey, Trans. Faraday Soc. 61, 674(1965).

19. W. Tsang and R.F. Hampson, J. Phys. Chem. Ref. Data 15, 1087(1986).

20. B. Veyret and R. Lesclaux, J. Phys. Chem. 85, 1918(1981).

21. R.S. Timonen, E. Ratajczak and D. Gutman, to be published.

22. F. Westley, Tables of Recommended Rate Constants for Chemical Reactions Occurring in Combustion, NSRDS-NBS67, 1980.

Note added in proof:

Recently, a similar study on $CH_3 + NO_2$ has been made at 443 K by A.P. Ballod, L.I. Poroikova, N.L. Shlyapnikova, and V.Y. Shtern (Kinet. Katal., 27, 1285(1986)), using di-t-butyl peroxide as the source of CH_3. Without a detailed modelling, they arrived at the following rate constant ratios:

$k_3/k_4 = 1.9 \pm 0.1$

$k_9/k_3 = 0.22 \pm 0.025$

$k_{10}/k_4 = 0.05 \pm 0.025$.