# Modeling the Decomposition of Nitromethane, Induced by Shock Heating

Yi-Xue Zhang and S. H. Bauer\*

Department of Chemistry, Baker Chemical Laboratory, Cornell University, Ithaca, New York 14853 Received: February 26, 1997; In Final Form: April 15, 1997<sup>®</sup>

The decomposition of nitromethane was studied over the temperature range 1000-1100 K in reflected shock waves. CH<sub>3</sub>NO<sub>2</sub> and the reaction products were analyzed by gas chromatography. The derived gross rate constant and activation energy for the disappearance of CH<sub>3</sub>NO<sub>2</sub> is consistent with that of Glänzer and Troe. A reaction mechanism consisting of 99 chemical reactions was developed to simulate the experimental data of the present study and that of Hsu and Lin. Good agreement between experiments and simulations was achieved. It appears that significant amounts of CH<sub>3</sub>NO<sub>2</sub> are destroyed through secondary reactions that involved highly reactive free radicals (H, OH, and CH<sub>3</sub>), suggesting the need for redeterming the *true* unimolecular decay rate constant for CH<sub>3</sub>NO<sub>2</sub>. For improvement of the performance of the model, several other rate constants also need to be determined. The final section is a preliminary report on a spectrophotometric technique for measuring the loss of nitromethane due to pyrolysis by recording its absorption of UV radiation, *directed axially* along a small diameter shock tube. Although only semiquantitative data were obtained, this novel procedure merits discussion.

## I. Introduction

The gas phase kinetics and mechanism of the thermal decomposition of organic—nitro compounds have been investigated by numerous authors.<sup>1–5</sup> These compounds are highly energetic and are commonly used as explosives and propellants.<sup>6</sup> Kinetic and mechanistic information on their decomposition pathways are critical for understanding their physical and chemical properties and particularly the environmental consequences of their extremely complex reactions in the atmosphere.

The first kinetic investigation of the decomposition of highly diluted  $CH_3NO_2$  in the gas phase *via* shock heating was carried out by Glänzer and Troe.<sup>7</sup> The reaction was studied over the temperature range 900–1400 K by following concentration changes of  $CH_3NO_2$  and  $NO_2$ , spectrophotometrically; other products were not determined. They assumed that the pyrolysis could be adequately described by the following three reactions.

$$CH_3NO_2 \rightarrow CH_3 + NO_2 \tag{1}$$

$$CH_3NO_2 + M \rightarrow CH_3 + NO_2 + M$$
 (2)

$$CH_3 + NO_2 \rightarrow CH_3O + NO$$
 (12)

The rate constants of reactions 1 and 2 were determined from first order decay curves for  $CH_3NO_2$ , over a range of temperatures and initial nitromethane and argon concentrations. They found that the reaction was in the fall-off region. The derived limiting low- and high-pressure rate constants are

$$k_0/(\text{cm}^3/(\text{mol}\cdot\text{s})) = 10^{17.1}[\text{Ar}] \exp\{(-42 \text{ kcal/mol})/RT\}$$
  
 $k_{\infty}/\text{s}^{-1} = 10^{16.25} \exp\{(-58.5 \pm 10.5 \text{ kcal/mol})/RT\}$ 

For reaction 12 the value  $1.3 \times 10^{13} \text{ cm}^3/(\text{mol}\cdot\text{s})$  was found by fitting the recorded [NO<sub>2</sub>] vs time curves to the above reactions.

Perche, et al.<sup>8,9</sup> investigated the pyrolysis of  $CH_3NO_2$  over the temperature range of 676–771 K, in a static reaction vessel. The content of the reactor was sampled periodically and analyzed by gas chromatography. They found numerous (clearly secondary) products: CO, NO,  $CH_4$ ,  $H_2$ ,  $C_2H_6$ ,  $CH_3$ -OH, HCN, CO<sub>2</sub>,  $CH_2O$ ,  $H_2O$ , and  $N_2$ . The time dependent concentrations were accounted for by a proposed mechanism of 28 reactions. Their numerical simulations matched the experimental data.

Hsu and Lin<sup>10</sup> followed the pyrolysis of CH<sub>3</sub>NO<sub>2</sub> over the temperature range 940-1520 K in a shock tube, over the pressure range of 0.4-2 atm, and monitored the appearance only of NO and CO in the reflected shock region with a frequency stabilized continuous wave (cw) CO laser. They suggested a mechanism of 37 reactions that was an extension of the mechanism of Perche and Lucquin.<sup>9</sup> A large body of kinetic data could thus be fitted reasonably well, provided that a rate constant of  $1.2 \times 10^{12}$  cm<sup>3</sup>/(mol·s) was chosen for the reaction between CH<sub>4</sub> and CH<sub>2</sub>O. However, this value, together with the previously determined rate constants at lower temperatures,<sup>11</sup> leads to an Arrhenius plot that very sharply curves upward above 1000 K. Whereas a nonlinear shape was later indicated by the experimental data of Choudhury et al.,<sup>12</sup> the magnitude of curvature was much smaller. At 1050 K, the measured rate constant is 30-fold smaller than that predicted by the earlier mechanism of Hsu and Lin.<sup>10</sup>

Here we report on the decomposition of CH<sub>3</sub>NO<sub>2</sub> developed in reflected shock waves. Our attention was focused on the rate of disappearance of CH<sub>3</sub>NO<sub>2</sub> and on the production rates of several light hydrocarbons over the temperature range 1000– 1100 K. To account fully for the totality of available data, a reaction mechanism of 99 reactions is proposed. Simulations based on this mechanism account very well for the kinetic data we derived and for the results reported by Hsu and Lin,<sup>10</sup> by Glänzer and Troe,<sup>7</sup> and Perche et al.<sup>8,9</sup>

### **II. Experimental Section**

We used a stainless steel, heatable shock tube, 1 in. i.d. The lengths of the driver and driven sections are 120 and 170 cm long, respectively. A damp tank is located on the driven section side next to the diaphragm holder. Shocks were generated by increasing the pressure of the He driver until the mylar diaphragm broke. Typical pressures on the driver (He) and driven sides are 80 psig and 300–400 Torr of ~0.6% CH<sub>3</sub>NO<sub>2</sub> in Ar, respectively. Two piezoelectric pressure sensors are

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**Figure 1.** Experimental (symbols) and simulation (lines) for the decomposition of CH<sub>3</sub>NO<sub>2</sub> over the temperature range 1000–1100 K. Conditions:  $[CH_3NO_2]_0 = 3.7 \times 10^{-4}$  M; [Ar] = 0.055 M; heating time, 1500  $\mu$ s. Symbols: (O) CH<sub>3</sub>NO<sub>2</sub>; ( $\bullet$ ) CH<sub>4</sub>; ( $\triangle$ ) C<sub>2</sub>H<sub>6</sub>; ( $\nabla$ ) C<sub>2</sub>H<sub>4</sub>; ( $\Box$ ) C<sub>2</sub>H<sub>2</sub>. The rate constant of reaction 2 was from line 5 of Figure 2, and  $k_1$ ,  $k_3$ , and  $k_4$  were chosen to be 0 in the simulations.

stationed 10 cm apart at the end of the driven section. Their combined signal was recorded and digitized through Biomation 8100 and Northern Tracor Signal Analyzer and stored in an IBM AT computer. The effective heating time was defined as the elapsed time from the beginning of the reflected shock wave to the point where the pressure signal was 80% of that of the reflected shock region. The storage tank, gas handling line, and the shocked tube were maintained at ~100 °C throughout the experiments. Nitromethane from Aldrich was used without further purification. High-purity helium and argon were the driving and carrier gases. Research grade methane, ethane, ethylene, and acetylene gases, used for GC calibration were from Matheson.

Immediately after each shock, a 16 mL sample was collected through the sampling valve located at the end of the driven section and analyzed via a Nicolet GC/9630 (Nicolet/IBM Instrument Inc.) with a flame ionization detector. The packed GC column Carbograph I (from Alltech) separated the hydrocarbons. Injector and detector temperatures were typically set at 250 °C, and the initial column temperature was 45 °C for the first 3 min. That temperature was increased at a rate of 20 °C/min until it reached the final temperature of 275 °C. The chromatograms were recorded with a Hewlett-Packard 3396A integrator. The following species were detected and wellseparated: CH<sub>3</sub>NO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>2</sub>. Radical scavengers were not introduced because we wish to determine the evolution of the overall pyrolysis, including secondary reactions.

### **III. Results and Discussions**

The percentage conversion of  $CH_3NO_2$  and the products distribution from GC analysis are plotted in Figure 1. The production of  $CH_4$  and  $C_2H_6$  has been reported,<sup>8,13</sup> but that of  $C_2H_4$  and  $C_2H_2$  has not been mentioned. When the temperature was increased, more  $CH_4$ ,  $C_2H_4$ , and  $C_2H_2$  were generated, whereas  $C_2H_6$  passed through a maximum and then decreased. Since the interactions among these four species and their radicals comprise the most important and exhaustively studied reactions



**Figure 2.** Arrhenius plots for reaction 1. Symbols are derived from our experiments. Lines 1, 2, and 4 are from Glänzer and Troe;<sup>7</sup> Ar concentrations are  $1.5 \times 10^{-3}$ ,  $1.0 \times 10^{-2}$ , and  $8.0 \times 10^{-2}$  M, respectively. Line 3 is the least squares fit to our data; values from line 5 were used for reaction 2 in Table 1 for simulating the experimental results in Figure 1.

in combustion chemistry, the roles they play in the pyrolysis of  $CH_3NO_2$  may be critical for understanding this complex system.

To compare our experimental data with those of Glänzer and Troe,<sup>7</sup> an Arrhenius plot based on our data is presented for comparison with plots of Glänzer and Troe in Figure 2. The vertical axis is the logarithm of the observed pseudo-first-order decay rate constant of CH<sub>3</sub>NO<sub>2</sub> divided by the concentration of the bath gas. In the figure lines 1, 2, and 4 are from Glänzer and Troe,<sup>7</sup> line 3 is the least squares fit to our experimental values, and line 5 is the rate constant for reaction 2 used in our simulations. The justification for using line 5 instead of the experimentally measured values (line 3) will be made clear below. The Arrhenius line for the experimental data is given by  $1.977 \times 10^{12} \exp\{[-(38 \pm 3) \text{ kcal/mol}]/RT\}$  (s<sup>-1</sup>). The activation energy is a few kilocalories smaller than that of Glänzer and Troe.<sup>7</sup> The reason for the discrepancy may be due to the relatively large scatter of our data. [We have not found a suitable reference reaction to add to our system without disturbing the overall reaction kinetics.] Over the temperature range shown in Figure 2 the rate constant is in the fall-off range: the low- and high-pressure limiting rate constants were derived by Glänzer and Troe<sup>7</sup> on the basis of their extensive experimental data. However, a unified expression that takes into account the entire fall-off behavior has not been reported.

Mechanism of the Reaction. The reaction mechanism we used to simulate the experimental data is compiled in Table 1. The NIST Chemical Kinetics Database<sup>14</sup> was the primary reference for the inserted rate expressions. The full mechanism was used to simulate all of the experimental results. Then the mechanism was simplified with the aid of a sensitivity analysis, after all the experimental results were satisfactorily explained. The rate constant of reaction 34, which is identified as a critical reaction in Hsu and Lin's mechanism to reproduce the experimentally determined CO production rate, was updated from the original  $1.2 \times 10^{12}$  cm<sup>3</sup>/(mol·s) to the experimentally determined values of  $10^{-12.05}T^{7.4} \exp(483/T)$  (cm<sup>3</sup>/(mol·s), a 30-fold decrease at temperatures above 1000 K. In our mechanism, several other routes for CO production were identified. The most important appears to be the unimolecular decomposition of CH<sub>2</sub>O, the rate constant of which was determined experimentally by Miyauchi et al.<sup>15</sup>

$$CH_2O + M \rightarrow H_2 + CO + M \tag{95}$$

 TABLE 1: CH<sub>3</sub>NO<sub>2</sub> Decomposition Mechanism<sup>a</sup>

no.	reaction	Α	n	$E_{\rm a}/R$	ref
1	$CH_3NO_2 \rightarrow CH_3 + NO_2$	$1.78 \times 10^{16}$	0	29 439	7
2	$CH_3NO_2 + M \rightarrow CH_3 + NO_2 + M$	$1.26 \times 10^{14}$	0	21 137	7
3	$CH_3 + NO_2 \rightarrow CH_3NO_2$	$2.07 \times 10^{10}$	-0.6	0	24
4	$CH_3 + NO_2 + M \rightarrow CH_3NO_2 + M$ $CH_4 + NO_2 \rightarrow CH_2ONO_2$	$3.59 \times 10^{14}$	-6	0	24
5	$CH_3 \rightarrow CH_3ONO$ $CH_3ONO \rightarrow CH_2O + NO$	$6.31 \times 10^{15}$	0	20 733	25
7	$CH_3ONO + M \rightarrow CH_3O + NO + M$	$2.29 \times 10^{13}$	0	15 298	20
8	$CH_3 O + NO \rightarrow CH_3 ONO$	$1.21 \times 10^{10}$	0	0	28
9	$CH_3 ONO \rightarrow CH_2O + HNO$	$3.98 \times 10^{13}$	0	19 374	29
10	$CH_3 ONO + M \rightarrow CH_2O + HNO + M$	$4.63 \times 10^{09}$	0	0	30
11	$CH_3NO_2 + CH_3 \rightarrow CH_4 + CH_2NO_2$	$2.40 \times 10^{10}$	0	4 529	10
12	$CH_3 + NO_2 \rightarrow CH_3O + NO$ $CH_2 + CH_2 \rightarrow C_2H_2$	$1.3 \times 10^{10}$ 1.09 × 10^{11}	-1.18	329	/ 16 <sup>b</sup>
14	$CH_3 + CH_3 + M \rightarrow C_2H_6 + M$	$1.09 \times 10^{18}$ $1.28 \times 10^{18}$	-7.03	1 390	16 <sup>b</sup>
15	$C_2H_6 + CH_3 \rightarrow CH_4 + C_2H_5$	$5.5 \times 10^{11}$	0	10 820	10
16	$NO_2 + NO_2 \rightarrow N_2O_4$	$5 \times 10^{8}$	-1.1	0	32
17	$NO_2 + NO_2 + M \rightarrow N_2O_4 + M$	$5.08 \times 10^{8}$	-3.8	0	32
18	$N_2O_4 \rightarrow 2NO_2$	$7.69 \times 10^{15}$	-1.1	6 460	32
19	$N_2O_4 + M \rightarrow 2NO_2 + M$ $NO_4 + NO_4 \rightarrow NO_4 + NO_4$	$7.76 \times 10^{10}$	-3.8	0 400 10 530	32
20	$NO_2 + NO_2 \rightarrow 2NO_2$	$8 \times 10^9$	0.75	10 550	34
22	$CH_3 + NO + M \rightarrow CH_3NO + M$	$8.89 \times 10^{12}$	-5.24	1 902	10
23	$NO_2 + NO \rightarrow N_2O_3$	$4.66 \times 10^{9}$	1.4	0	36
24	$CH_3O + CH_3O \rightarrow CH_3OH + CH_2O$	$1.1 \times 10^{10}$	0	0	10
25	$CH_3O + NO_2 \rightarrow CH_3ONO_2$	$1.21 \times 10^{7}$	0	0	37
26	$CH_3O + NO_2 + M \rightarrow CH_3O NO_2 + M$ $CH_3ONO_2 \rightarrow CH_3O + NO_2$	$3.2/ \times 10^{13}$	0	16 802	56 28
27	$CH_3ONO_2 \rightarrow CH_3O + NO_2$ $CH_2O + NO_2 \rightarrow CH_2O + HNO_2$	$1 \times 10^{-1}$ $4 0 \times 10^{8}$	0	10 802	38 10
29	$CH_3OH + NO_2 \rightarrow CH_2OH + HNO_2$	$2 \times 10^{9}$	ů 0	11 372	40
30	$2HNO_2 \rightarrow H_2O + NO + NO_2$	$5.71 \times 10^{2}$	0	0	41
31	$CH_3OH + CH_3 \rightarrow CH_4 + CH_3O$	$6.75 \times 10^{5}$	3.1	3 490	43
32	$CH_3OH + CH_3 \rightarrow CH_4 + CH_2OH$	$2.64 \times 10^{6}$	3.2	3609	43
33	$CH_2OH + CH_4 \rightarrow CH_3OH + CH_3$	$1.01 \times 10^{6}$	3.1	8 166	43
34 35	$CH_3 + CH_2O \rightarrow CH_4 + HCO$ $CH_4 + NO_2 \rightarrow CH_2 + HNO_2$	$1.82 \times 10^{3}$ $1.2 \times 10^{10}$	7.4 0	-485	12
36	$NO_2 + HNO_2 \rightarrow NO + HNO_3$	$6.03 \times 10^{-2}$	0	15 097	44
37	$CH_2O + NO_2 \rightarrow HCO + HNO_2$	$2.95 \times 10^{8}$	0	6 470	46
38	$CH_3O + CH_4 \rightarrow CH_3OH + CH_3$	$1.57 \times 10^{8}$	0	4 450	31
39	$NO_2 + NO_2 \rightarrow NO + NO + O_2$	$1.63 \times 10^{9}$	0	13 147	33
40	$HCO + CH_4 \rightarrow CH_3 + CH_2O$	$8.18 \times 10^{7}$	2.85	11 330	31
41	$CH_3 + HCO \rightarrow CH_4 + CO$ $CH_4 + HCO \rightarrow CH_2 CHO_2$	$1.21 \times 10^{11}$ $1.81 \times 10^{10}$	0	0	31
43	$CH_2 CHO \rightarrow CH_2 + HCO$	$2 \times 10^{15}$	0	39 811	47
44	$HCO + CH_2OH \rightarrow CO + CH_3OH$	$1.21 \times 10^{11}$	Ő	0	43
45	$HCO + CH_2OH \rightarrow CH_2O + CH_2O$	$1.81 \times 10^{11}$	0	0	43
46	$CH_3 + CH_3O \rightarrow CH_4 + CH_2O$	$2.41 \times 10^{10}$	0	0	31
47	$CH_3CHO + NO_2 \rightarrow HNO_2 + CH_3CO$	$3.12 \times 10^{8}$	0	13 632	48
48	$CH_3OH + NO_2 \rightarrow HNO_2 + CH_2OH$ $CH_OH + HCO \rightarrow CH_O + CH_OH$	$2 \times 10^{\circ}$ 1 45 × 10 <sup>8</sup>	0	6 506	40
49 50	$HCO + NO \rightarrow CO + HNO$	$3.453 \times 10^{9}$	2.9	1 007	31
51	$HCO + HNO \rightarrow NO + CH_2O$	$6.03 \times 10^{8}$	0	1 000	33
52	$CH_3O + CH_2OH \rightarrow CH_3OH + CH_2O$	$2.41 \times 10^{10}$	0	0	43
53	$CH_{3}O + CH_{3}CHO \rightarrow CH_{3}OH + CH_{3}CO$	$5 \times 10^{6}$	0	0	49
54	$CH_3O + HCO \rightarrow CH_3OH + CO$	$9.04 \times 10^{10}$	0	0	31
55 56	$CH_3O + HNO \rightarrow CH_3OH + NO$	$3.16 \times 10^{10}$ $1.02 \times 10^{8}$	0	1 500	50
50 57	$CH_3 + HNO \rightarrow CH_4 + NO$	$2 \times 10^9$	0	1 300	51
58	$CH_3 + CH_3CHO \rightarrow CH_4 + CH_2CHO$	$1.79 \times 10^{5}$	5.64	1 240	52
59	$CH_3 + CH_3 \rightarrow C_2H_4 + H_2$	$1.0 \times 10^{13}$	0	16 566	53
60	$CH_3 + CH_3 \rightarrow C_2H_5 + H$	$3.01 \times 10^{10}$	0	6 800	52
61	$C_2H_5 \rightarrow C_2H_4 + H$	$4.7 \times 10^{11}$	0	13 387	10
62	$C_{2}H_{5} + CH_{3}O \rightarrow CH_{2}O + C_{2}H_{6}$	$2.41 \times 10^{10}$	0	6 2 2 2	31
64	$C_2\Pi_5 + C\Pi_4 + C_2\Pi_6 + C\Pi_3$ $C_2\Pi_5 + C\Pi_2 \rightarrow C_2\Pi_5 + HCO$	$4.93 \times 10^{7}$	2.81	2 950	31
65	$C_2H_5 + CH_3 \rightarrow CH_4 + C_2H_4$	$1.13 \times 10^{9}$	-0.5	2 > 5 0	31
66	$C_2H_6 + CH_3O \rightarrow CH_3OH + C_2H_5$	$2.41 \times 10^{8}$	0	3 570	31
67	$CH_3NO_2 + H \rightarrow CH_3 + HNO_2$	$3.176 \times 10^{12}$	0	7 922	this work
68	$CH_3 + HNO_2 \rightarrow CH_4 + NO_2$	$2.142 \times 10^{14}$	0	10 052	this work
69 70	$H + C_2H_6 \rightarrow H_2 + C_2H_5$ CH Q + M $\rightarrow$ CH Q + H + M	$7.43 \times 10^{9}$	1.5	3 730	52
70 71	$CH_3O + M \rightarrow CH_2O + H + M$ $CH_2O + NO \rightarrow CH_2O + HNO$	$1.11 \times 10^{12}$ $3.2 \times 10^{9}$	-7.5	113/0	10
72	$CH_{3}O + OH \rightarrow CH_{2}O + H_{3}O$	$3.2 \times 10^{10}$ $3.2 \times 10^{10}$	0	0	10
73	$NO_2 + H \rightarrow NO + OH$	$2.9 \times 10^{11}$	ő	407.6	10
74	$CH_3 + OH \rightarrow CH_2O + H_2$	$8.0 \times 10^9$	0	0	10
75	$CH_3 + OH \rightarrow CH_3O + H$	$2.0 \times 10^{13}$	0	13 790	10
76	$CH_3NO_2 + H \rightarrow CH_2NO_2 + H_2$	$3.469 \times 10^{9}$	1.27	1 329	10

**TABLE 1 (Continued)** 

no.	reaction	Α	n	$E_{\rm a}/R$	ref
77	$CH_3NO_2 + OH \rightarrow CH_2NO_2 + H_2O$	$2.325 \times 10^{7}$	2.48	-1 218	10
78	$CH_2NO_2 \rightarrow CH_2O + NO$	$1.0 \times 10^{13}$	0	18 120	10
79	$CH_3 NO \rightarrow HCN + H_2O$	$7.9 \times 10^{9}$	0	19 780	10
80	$CH_3 NO + M \rightarrow CH_3 + NO + M$	$8.447 \times 10^{20}$	-6.85	24 360	10
81	$CH_2O + H \rightarrow HCO + H_2$	$3.469 \times 10^{12}$	1.27	1 329	10
82	$CH_2O + OH \rightarrow HCO + H_2O$	$2.486 \times 10^{08}$	2.65	-956.2	10
83	$HNO + M \rightarrow H + NO + M$	$2.9 \times 10^{13}$	0	24 560	10
84	$H_2 + OH \rightarrow H_2O + H$	$5.2 \times 10^{10}$	0	3 271	10
85	$H_2O + H \rightarrow H_2 + OH$	$2.2 \times 10^{11}$	0	10 970	10
86	$HNO_2 + M \rightarrow NO + OH + M$	$5.068 \times 10^{17}$	-3.86	26 320	10
87	$HCO + M \rightarrow CO + H + M$	$1.6 \times 10^{11}$	0	7 398	10
88	$HCO + NO_2 \rightarrow HNO_2 + CO$	$1.0 \times 10^{11}$	0	0	10
89	$\rm CO + OH \rightarrow H + CO_2$	$1.037 \times 10^{8}$	1.3	-385	10
90	$\rm CO + NO_2 \rightarrow NO + CO_2$	$1.9 \times 10^{9}$	0	14 750	10
91	$C_2H_6 + OH \rightarrow H_2O + C_2H_5$	$6.3 \times 10^{10}$	0	1 812	10
92	$C_2H_5 + NO_2 \rightarrow CH_3 + CH_2O + NO$	$1.3 \times 10^{10}$	0	0	10
93	$C_2H_4 + OH \rightarrow CH_2O + CH_3$	$5.0 \times 10^{9}$	0	0	10
94	$CH_4 + OH \rightarrow CH_3 + H_2O$	$3.2 \times 10^{10}$	0	2 516	10
95	$CH_2O + M \rightarrow CO + H_2 + M$	$2.1 \times 10^{13}$	0	17 620	15
96	$N_2O_3 \rightarrow NO + NO_2$	$4.577 \times 10^{16}$	0	2 456	36
97	$C_2H_4 + H \rightarrow C_2H_3 + H_2$	$2.41 \times 10^{9}$	2.53	6 160	31
98	$C_2H_3 + H_2 \rightarrow C_2H_4 + H$	$9.71 \times 10^{7}$	2.63	4 298	31
99	$C_2H_3 \rightarrow C_2H_2 + H$	$2.0 \times 10^{14}$	0	20 000	52

<sup>*a*</sup> Rate expression in the mechanism is in the form of  $A(T/298)^n \exp(E_a/RT)$ . The unit of rate constant is  $M^{-(m-1)} s^{-1}$ , where *m* is the order of the reaction. <sup>*b*</sup>  $F_{cent} = 0.381 \exp(-T/73.2) + 0.619 \exp(-T/1180)$ .

Because of its importance in combustion chemistry, the recombination reaction of  $CH_3$  radicals has been studied extensively; the most reliable rate constant seems to be that of Slagle et al.<sup>16</sup> Rate constants for the branching reactions have been debated. However, since they are only important at much higher temperatures, these reactions are not critical under our experimental conditions.

To derive the consequences of the mechanism listed in Table 1, we used the program Livermore-solver for ordinary differential equations (LSODE) developed by Alan C. Hindmarsh. A relative error tolerance of  $10^{-3}$  was found to be sufficient to give accurate results from the integrator. We first integrated the differential equations that express the mechanism at the measured reflected shock temperatures up to the measured effective heating times and then lowered the reaction temperature to  $\sim 100$  °C (temperature of the heated shock tube) and continued the integration for one more minute. The second part of the integration reflects the contribution from reactions of unquenched radicals during the cooling wave. These calculations indicated that the added effects are negligible. Therefore, for most of the calculations presented in this work only the first part of the integrations was performed. Since a unified expression for the fall-off curve for the unimolecular CH<sub>3</sub>NO<sub>2</sub> decomposition is not available, the experimental values from line 3 of Figure 2 were used initially for  $k_2$  in place of reactions 1-4, to fit the experimental data in Figure 1. It was soon discovered, however, that this value for  $k_2$  leads to much greater extents of reaction than those measured. The decay of CH3- $NO_2$  is not really a unimolecular process. In fact about 40% of the CH<sub>3</sub>NO<sub>2</sub> is lost to secondary reactions due to attack of CH<sub>3</sub>NO<sub>2</sub> by free radials (H, OH, and CH<sub>3</sub>) generated in the subsequent reactions. The overall reaction is a chain process, but the chain length is rather short. We then fitted the experimental data with  $k_2$  as an adjustable parameter. These values are represented by line 5 in Figure 2. The fact that lower values for  $k_2$  need to be used to fit the experimental data suggest that values of  $k_1$  and  $k_2$  reported by Glänzer and Troe are too large.

There are two channels for the reaction between  $CH_3NO_2$ and H. One leads to  $CH_2NO_2$  and  $H_2$  (reaction 76) and the other to  $CH_3$  and  $HNO_2$  (reaction 67). The rate of the second channel was studied by Thomsen et al.<sup>18</sup> at 298 K; they found that it accounts for about 70% of the reaction. We assumed that it is also important over the temperature range covered in this work and chose the expression  $3.18 \times 10^{12} \exp(-7922/T)$  for the best fit of our experimental data. The rate constant for the reaction between CH<sub>3</sub> and HNO<sub>2</sub> has not been reported, We choose  $k_{68} = 2.142 \times 10^{14} \exp(-10052/T)$  (M<sup>-1</sup> s<sup>-1</sup>), which is comparable to rate constants for several analogous reactions.

To account for the production rates of CO and NO, Hsu and  $Lin^{10}$  used values of  $k_2$ , given by line 1 in Figure 2, which was suitable for the density of gases in their experiments. Simulation of the data of Hsu and Lin with the reactions in Table 1 are shown in Figure 3. Our mechanism correctly simulates the measured CO production rate using the rate constant for [CH<sub>3</sub> + CH<sub>2</sub>O], which is about 30-fold smaller than that of Hsu and Lin. Because of the larger rate constant, their mechanism predicts a larger production of CH<sub>4</sub> than that observed (Figure 1). The major discrepancy between simulation and experiment is the production of NO at low temperatures ( $\sim$ 1050), where the predictions are noticeably smaller than the measured values. This is partially inherited form the mechanism of Hsu and Lin.<sup>10</sup> Since the major portion of NO is formed at early times from the reaction of  $[CH_3 + NO_2 \rightarrow CH_3O + NO]$ , the reliability of this rate constant is critical for successfully modeling the NO kinetics.

Figure 4 shows the kinetic behaviors of all chemical species in the reaction at 1090 K, for  $[CH_3NO_2]_0 = 3.7 \times 10^{-4}$  M. The major chemical species are CH<sub>3</sub>NO<sub>2</sub>, CO, NO, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, CH<sub>2</sub>O, NO<sub>2</sub>, HCN, H<sub>2</sub>O, and CO<sub>2</sub>. Of particular interest are the [CH<sub>3</sub>NO<sub>2</sub>] and [NO<sub>2</sub>] vs time curves. Glänzer and Troe<sup>7</sup> followed the changes of these two species and derived rate constants of reactions 1, 2 and 12 by assuming that the reaction occurred mainly through these three steps; i.e., the disappearance of CH<sub>3</sub>NO<sub>2</sub> was unimolecular. We have shown that the decay of CH<sub>3</sub>NO<sub>2</sub> is complicated by direct reactions between the free radicals formed during the pyrolysis and the remaining CH<sub>3</sub>-NO<sub>2</sub>. Since this effect is sufficiently large, we questioned the reliability of the rate constants they determined. However, the [CH<sub>3</sub>NO<sub>2</sub>] vs time curve from simulations does remain close to a first-order decay process, as shown in Figure 5 a, where the dotted line are the least squares fit to the logarithm of the CH<sub>3</sub>NO<sub>2</sub> concentration. Comparison of the NO<sub>2</sub> profile derived from the mechanism of Table 1, and that due only to reactions



**Figure 3.** Experimental data (symbols) of Hsu and Lin<sup>10</sup> and simulations from the mechanism in Table 1 for CO and NO in the CH<sub>3</sub>NO<sub>2</sub> decomposition reactions.  $k_2 = 4.2 \times 10^{16} \exp\{(-42 \text{ kcal/mol})/RT\}$  (cm<sup>3</sup>/(mol s)) for reaction 2 was used in the simulations.

1, 2, and 12 with the appropriate rate constants for (1) and (2) (see Figure 5b), suggests that the assumption that NO<sub>2</sub> reacts mainly with  $CH_3$  made by Glänzer and Troe<sup>7</sup> might also be an oversimplification. Therefore, it appears that a redetermination of the rate constant of reaction 12 should be undertaken.

Sensitivity Analysis and Simplification of the Reaction Mechanism. Over the past decades, sophisticated mathematical methods have been developed to identify the important reactions and to reveal their roles in complicated reaction networks.<sup>19,20</sup> We utilized the method of principal component analysis developed by Turanyi et al.<sup>21</sup> A brief outline of the method is presented in the Appendix. The program package KINAL<sup>22</sup> was used to analyze the mechanism in Table 1, at several



**Figure 4.** Computed kinetic behaviors of all chemical species appearing in the mechanism of Table 1. T = 1090 K. All other conditions are the same as those in Figure 1. Numbers in the figure represent chemical species. They are as follows: 1, NO; 2, H<sub>2</sub>; 3, CO; 4, H<sub>2</sub>O; 5, CH<sub>4</sub>; 6, C<sub>2</sub>H<sub>6</sub>; 7, C<sub>2</sub>H<sub>4</sub>; 8, CO<sub>2</sub>; 9, HCN; 10, HNO<sub>2</sub>; 11, OH; 12, CH<sub>2</sub>NO<sub>2</sub>; 13, C<sub>2</sub>H<sub>2</sub>; 14, CH<sub>3</sub>CHO; 15, CH<sub>3</sub>NO; 16, CH<sub>2</sub>CHO; 17, CH<sub>3</sub>OH; 18, O<sub>2</sub>; 19, C<sub>2</sub>H<sub>3</sub>; 20, CH<sub>2</sub>OH; 21, CH<sub>3</sub>CO; 22, N<sub>2</sub>O<sub>3</sub>; 23, HNO<sub>2</sub>; 24, N<sub>2</sub>O<sub>4</sub>; 25, CH<sub>3</sub>NO<sub>2</sub>; 26, CH<sub>2</sub>O; 27, NO<sub>2</sub>; 28, CH<sub>3</sub>; 29, HNO; 30, H; 31, C<sub>2</sub>H<sub>5</sub>; 32, HCO; 33, CH<sub>3</sub>O NO<sub>2</sub>; 34, CH<sub>3</sub>O; 35, CH<sub>3</sub>ONO; 36. NO<sub>3</sub>.

temperatures and initial CH<sub>3</sub>NO<sub>2</sub> and Ar concentrations. In each case, several points distributed throughout the duration of the reaction were chosen for analysis. Table 2 shows the results of such an analysis for a reaction at 1090 K, with  $[CH_3NO_2]_0 = 3.7 \times 10^{-4}$  M and [Ar] = 0.055 M, at four reaction times:  $5 \times 10^{-6}$ ,  $2 \times 10^{-5}$ ,  $3 \times 10^{-4}$ , and  $1.5 \times 10^{-3}$  s. For each reaction time, the KINAL principal component analysis leads to a set of eigenvalues and associated eigenvectors. Each eigenvector contains a group of elements of relatively large



**Figure 5.** Kinetic behavior of CH<sub>3</sub>NO<sub>2</sub> and NO<sub>2</sub> from simulations. All conditions are the same as those in Figure 4. Solid lines in both a and b are from simulations based on the mechanism in Table 1. The dashed line in a is the least squares fit to the solid line. The dashed line in b is from a simulation with a mechanism that consists only of reactions 2 and 12, with the rate constant  $k_2$  that is calculated from a and the rate constant for (12) of  $1.3 \times 10^{10}$  M<sup>-1</sup> s<sup>-1</sup>.

magnitude that identify the major reactions that correspond to the associated eigenvalues. Reactions that lead to only small

TABLE 2: Principal Component Analysis at Four Points during the Reaction<sup>a</sup>

elements in all eigenvectors, or to large elements in eigenvectors but are associated with small eigenvalues, may be eliminated from the mechanism. A reaction is considered essential if it belongs to a reaction group with eigenvalues  $> 10^{-4}$ , and the elements in the corresponding eigenvectors exceed 0.1.

The principal component analysis in Table 2 indicates that there are 40 reactions that are not important, and these reactions may be eliminated from the mechanism without affecting the kinetic behaviors of any of the chemical species in the system. Simulations carried out with the reduced mechanism showed that this is indeed the case. Deviations in species concentrations remain less than 5% for all species except for CH<sub>3</sub>CHO (~14%) and OH ( $\sim$ 10%). The mechanism can be further simplified by noting that several species are in rapid equilibrium with other species during the entire reaction. These are CH<sub>3</sub>ONO<sub>2</sub>, N<sub>2</sub>O<sub>3</sub> and N<sub>2</sub>O<sub>4</sub>, CH<sub>3</sub>NO. Therefore, reaction pairs 26,27; 23, 96, and 22, 80 are also redundant. Some reactions are important only in parts of the reactions sequence. Their influence can be tested by trial and error. It should be pointed out that the analysis was carried out by assuming that all of the species are major. The reduced mechanism is the minimum required to reproduce the concentration profiles of all of the species. However, in practice only a few of the total species in a complex chemical system are measurable, so that the immediate goal is to reproduce their behaviors. When this restriction is applied, the mechanism may be further simplified. The simplified mechanism can be compared with those of Hsu and Lin and of Perche et al. All 37 reactions of the Hsu and Lin set were included in Table 1. We found that 11 of them are not important in any parts of the reaction and therefore can be deleted; 3 of

reaction	$t = 5 \times 10^{-6} sec$	$t = 2 \times 10^{-5} sec$	$t = 3 \times 10^{-4} \text{ sec}$	$t = 1.5 \times 10^{-3} \text{ sec}$	50				
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18					68				
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<sup>a</sup> Temperatures and other conditions are as in Figure 4. Important reactions are shaded in the table.

TABLE 3: Dominant Reactions of Different Species during the Reaction<sup>a</sup>

species	$t = 5 \times 10^{-6} \mathrm{s}$	$t = 2 \times 10^{-5} \mathrm{s}$	$t = 3 \times 10^{-4} \mathrm{s}$	$t = 1.5 \times 10^{-3} \mathrm{s}$
CH <sub>3</sub> NO <sub>2</sub>	2,76	2, 76, 77, 67	2, 76, 67, 77	2, 76, 67
CH <sub>4</sub>	11, 68	68, 11	68, 94	68, 94, 15, 57
$C_2H_6$	13	13	13, 91	13, 69, 91
$\tilde{C_2H_4}$	61	61	61, 93	61, 93
$C_2H_2$	99	99	99	99
CO	95	95, 87	95, 87	95, 89
NO	12, 78, 73	12, 78, 73	12, 73, 78, 22, 70	22, 80, 73, 12, 78
$NO_2$	2, 12	2, 12, 73	2, 12, 73, 68	2, 73, 12
CH <sub>3</sub>	2, 12, 13	2, 12, 13, 67	2, 12, 13, 68, 67, 22, 80	22, 80, 2, 12, 13
Н	70, 76, 67, 73	70, 76, 73, 67	70, 73, 76, 87, 67, 84	73, 70, 84, 61, 76, 69, 67, 89, 58
OH	73, 77	73, 77, 82	73, 82, 84, 77, 91	73, 84, 91, 89
HCO	87, 82, 81, 34	87, 82, 81	87, 82, 81	87, 81, 82
CH <sub>2</sub> O	70, 78	70, 78, 95	95, 70, 78, 82	95, 70, 78
$C_2H_5$	60, 61	61, 91, 60	61, 91	61, 69, 91
$H_2$	76	76, 95	95, 76, 84	95, 84, 76, 69
$CO_2$	89	89	89	89
$C_2H_3$	97, 99	97, 99	97, 99	97, 99
$H_2O$	77	77, 82	82, 84, 77, 91	84, 91, 79, 94
$NO_3$	20	20, 21	21, 20	21, 20
$HNO_2$	67	67, 68	68, 67, 86	67, 68, 86
CH <sub>3</sub> O	12, 70	70, 12	12, 70	12, 70
$CH_2NO_2$	76, 78, 77	78, 76, 77	78, 76, 77	78, 76
CH <sub>3</sub> OH	55, 56	55, 56, 54	55	55, 32
CH <sub>3</sub> CO	47, 53	47, 53	47, 53	47
HCN	79	79	79	79
CH <sub>3</sub> ONO <sub>2</sub>	26, 27	26, 27	27, 26	27, 26
CH <sub>3</sub> CHO	42	42	42	58, 42
$O_2$	39	39	39	39
$CH_2OH$	32	32	32	32
$CH_2CHO$	58	58	58	58
$CH_3NO$	22, 80	22, 80	22, 80	22, 80
CH <sub>3</sub> ONO	5, 10	5, 10	10, 5, 8, 6	10, 5, 8, 6
HNO	10	10	50, 57, 10	57, 50, 83, 10
$N_2O_3$	23, 96	23, 96	23,96	23, 96
$N_2O_4$	16, 18	16, 18	16, 18	16, 18

<sup>a</sup> Temperature and other conditions are as in Figure 4.

them are only important in some parts of the reaction. The most striking difference between the present and Hsu-Lin mechanisms is that reaction 34 in Table 1 is crucial in their set, but its rate constant has to be raised by 30-fold in order to reproduce the experimental results on CO and NO. In the present mechanism no. 34 is important only in part of the reaction. The experimental data for CO and NO still can be reproduced equally well. Unlike the present mechanism, the Hsu and Lin mechanism performs poorly in reproducing the experimental results on light hydrocarbons. Among the 26 reactions in the Perche et al. mechanism we found that 12 of them are important in the present mechanism; the rate constants of most of these reactions were updated.

The results in Table 3 show the dominant reactions associated with each chemical species at several times during the reaction. Species associated with only one chemical reactions are usually inert products, while species associated with a pair of reaction are usually in rapid equilibrium or in a quasi-stationary state. The most reactive species are H and CH<sub>3</sub>; these lead to the chain.

# IV. Spectrophotometric Measurements: Test of a Technique

The experiments described below were designed to record time dependent absorption spectra of a pyrolyzing substance using a small-diameter shock tube. A well-focused beam is directed axially from the end of the driver section downstream through the shock heated gas, with conditions adjusted so that pyrolysis is limited to the reflected shock domain. This is an extension of the procedure described by Stephens and Bauer,<sup>54</sup> which was used to record IR and visible emissions from shock heated hydrocarbons. However, the conversion of recorded signals to rate constants is more involved for absorption than for emission spectra. To date, only semiquantitative rate constants were derived. We did demonstrate that under the conditions used for nitromethane no detectable photolysis by the incident radiation<sup>55</sup> occurred during the overall exposure of the driven sample to light emitted by the xenon arc lamp (Oriel no. 6256).

The emitted light was focused through the quartz rear shocktube window to a 5 mm "disk" at the position of the diaphragm, thus minimizing perturbation in the intensity that arises from flapping edges of the broken diaphragm. Downstream, at the end of the driven section, the emergent beam is focused onto the entrance slit of a grating monochromator (with suitable filters to eliminate stray light and overlapping orders). Signals from an IP28 photomultiplier and from the piezoelectric gauges were recorded simultaneously, digitized with Biomation 8100 and Tracor Northern NS-575A digital signal analyzer, and stored in an IBM AT computer. Typical records are shown in Figure 6 a (with only Ar in the test section) and Figure b (with 2%  $CH_3NO_2$ —Ar mixture). Fluctuations in the transmitted light intensity are probably due to the flapping of edges of the broken diaphragm. This effect is relatively small and can be corrected.

Modeling based on shock tube/GC data indicates that the disappearance of CH<sub>3</sub>NO<sub>2</sub> during pyrolysis, while not strictly unimolecular, remains pseudo-first order. Therefore, in the following analysis we assumed that an empirical first-order rate constant would be obtained from the experimental data. The voltage signal from the photomultiplier was converted to absorbance with  $A(t) = \ln (I_0/I)$ , where  $I_0$  and I are { $V(\text{dark}) - V(\text{CH}_3\text{NO}_2)$ }, respectively.

At any time after the incident shock arrived at the end plate (refer to Figure 7) the beam passes through a length  $x_2$  of sample at  $T_2$  (not reacted) and a length  $x_5$  at  $T_5$  over which some reaction



Figure 6. Recorded pressure and light intensity, typical scans: (a) Ar only; (b) 2% CH<sub>3</sub>NO<sub>2</sub> in Ar.

has occurred. Hence,

$$A(t) = \epsilon_5 [CH_3NO_2]_5^*(t) x_5(t) + \epsilon_2 [CH_3NO_2]_2 x_2(t)$$
 (I)

where subscripts 1, 2, and 5 refer to preshock, incident shock, and reflected shock regions and  $\epsilon_2$  and  $\epsilon_5$  are the extinction  $\exp(-k_u t)$ ] (II)

coefficients of CH<sub>3</sub>NO<sub>2</sub> in the respective regions. Since the extent of reaction in the reflected shock region depends on x,  $[CH_3NO_2]_5^*(t)$  represents a distance-integrated magnitude. For a unimolecular decay,

$$[CH_{3}NO_{2}]_{5}^{*}(t) = (1/u_{5}t) \int_{0}^{u_{5}t} [CH_{3}NO_{2}]_{1}(\rho_{5}/\rho_{1})$$
  

$$exp[(-k_{u}(1 - x/u_{5}t)t] dx$$
  

$$= (1/u_{5}t) \{ [CH_{3}NO_{2}]_{1}(u_{5}/k_{u})(\rho_{5}/\rho_{1})[1 - u_{5}(t)t] \}$$

where  $x_5$  has been replaced by  $u_5t$ ,  $u_5$  is the reflected shock speed, and  $\rho$  is the density. The term [CH<sub>3</sub>NO<sub>2</sub>]<sub>2</sub>x<sub>2</sub> in (I) is obtained from mass balance [l] is the total length of the driven section],

$$[CH_{3}NO_{2}]_{1}l = [CH_{3}NO_{2}]_{2}x_{2} +$$
  
total incident shock region  

$$[CH_{3}NO_{2}]_{5}\circ x_{5}$$
(III)  
reflected shock region  
if no reaction occurs  

$$[CH_{3}NO_{2}]_{2}x_{2} = [CH_{3}NO_{2}]_{1}l - [CH_{3}NO_{2}]_{5}\circ u_{5}t$$

= 
$$[CH_3NO_2]_1(l - (\rho_5/\rho_1)u_5t)$$
 (IV)

therefore

$$A(t) = \epsilon_2 [CH_3NO_2]_1 [l - (\rho_5/\rho_1)u_5 t] + \epsilon_5 [CH_3NO_2]_1 (u_5/k_u)(\rho_5/\rho_1) [1 - \exp(-k_u t)]$$
(V)

For nitromethane the temperature dependence of  $\epsilon$  at 230 nm has been experimentally determined by Glänzer and Troe<sup>7</sup> (Figure 8). We assume the same temperature dependence applies to 300 nm.  $u_5$  can be determined from the pressure



Figure 7. Wave diagram that is the basis for converting light intensity signals to time dependent absorbance.



Figure 8. Temperature dependence of extinction coefficients.



**Figure 9.** Comparison of  $k_u$  values derived spectrophotometrically (open circles) with the curve based on GC analyses (solid line).

trace in Figure 6, and  $\rho_5/\rho_1$  can be computed from the measured incident shock speed.

In the above equations  $t < t_{\text{max}}$ , where  $t_{\text{max}}$  is where the reflected shock is intersected by the interface. However, our experiments indicate that  $t_{\text{max}}$  is considerably shorter than the heating time indicated by the pressure trace;  $t_{\text{max}}$  is approximated by  $l/\{(\rho_5/\rho_1)u_5\}$ .

Experimental A(t) vs time curves were fitted to eq 7. Although the predicted curves resemble the experimental ones, quantitative agreement was not achieved. Per the fitted relation, the calculated peak absorbance always appeared earlier than the experimentally recorded times, indicating that the value of  $k_u$ used in fitting (7) was too large, whereas the predicted slope of the latter part of the curve was always smaller.

In Figure 9 magnitudes of  $k_u$  derived from the photometric measurements were plotted for comparison with the Arrhenius curve 3 (Figure 2). It is probable that the scatter is due in part to inaccurate estimates of  $T_5$ , which for these runs were computed from recorded reflected shock speeds.

### V. Conclusion

The reaction mechanism proposed in Table 1 reproduces our experimental results on the production of hydrocarbons, and those of Hsu and Lin on the kinetics of NO and CO. The net rate constant for the decay of  $CH_3NO_2$  is consistent with that of Glänzer and Troe. Overall, the pyrolysis of  $CH_3NO_2$  is found to be a chain process. About 40% of the nitromethane is lost through secondary reactions. Simulations with the proposed mechanism indicate that simple dilution cannot overcome this

problem, and the best way to determine the unimolecular decay of  $CH_3NO_2$  would be to add a large amount of radical scavengers to the system. The kinetic curve for  $NO_2$  derived from the extended mechanism is very different from the previously proposed mechanism, which was used by Glänzer and Troe to derive the rate constant of the reaction between  $CH_3$  and  $NO_2$ . To fully unravel this pyrolysis, it appears necessary to extend the temperature range over which the reaction is investigated and to identify and monitor more reaction intermediates and products.

The recorded time dependence of the absorption spectra in a small-diameter shock tube, using the axial incidence of radiation, did permit estimation of unimolecular rate constants within a factor of 3. This technique merits further developments.

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### Appendix

**Principal Component Analysis of the Rate Sensitivity Matrix.** Mathematical tools and their applications for analyzing complex kinetic systems have been thoroughly reviewed by Turanyi.<sup>19</sup> We applied the so-called principal component method to analyze the mechanism in Table 1. This procedure was discussed in several previous publications;<sup>19,21,23</sup> here, we present a brief outline.

In a homogenous isothermal chemical system, the reactions involved can be described by a set of ordinary differential equations.

$$d\mathbf{c}/dt = f(\mathbf{k}, \mathbf{c}) \tag{A1}$$

where  $\mathbf{c}(t)$  is the *n*-vector of species concentration with  $\mathbf{c}(t=0) = \mathbf{c}_0$  and  $\mathbf{k}$  is the *p*-vector of kinetic parameters. The basic quantity that determines concentration sensitivity is

$$S_{ii}(k_0, \mathbf{c}_0, t_1, t_2) = \partial \dot{c}_i(t_2) / \partial k_i \tag{A2}$$

which reflects the effect of a change in the value of the *j*th parameter in  $k_0$  at  $t_1$  on the values of  $c_i$  at  $t_2$ . For most chemical systems, direct differentiation of the kinetic equations in (A1) to obtain  $S_{ij}$  is impractical; it can be more readily obtained through numerical methods. The rate sensitivity matrix,

$$\mathbf{F}_{ii}(\mathbf{k}_0, \mathbf{c}_0, t) = \partial \dot{c}(t) / \partial k j \tag{A2'}$$

may be written in normalized form,

$$\mathbf{F}_{ij}(\mathbf{k}_0, \mathbf{c}_0, t) = \{\partial \ln f_i / \partial \ln k_j\} = \{v_{ij} R_j / f_j\}$$
(A3)

The v's in (A3) comprise the stiochiometric matrix,  $R_j$  the rate of reaction j, and  $f_i$  the production rate of species i. The rate sensitivity has the advantage of not having two time dependencies as in the case of local concentration sensitivity where both  $t_1$  and  $t_2$  need to be considered.

To evaluate the importance and the interdependence of the kinetic parameters, one must study the effect of parameter change on the concentrations of a group chemical species. This can be treated mathematically with the following objective function:

$$Q(\alpha,c) = \sum_{i=1}^{n} \left[ \frac{f_i(\alpha,c) - f_i(\alpha_0,c)}{f_i(\alpha_0,c)} \right]^2$$
(A4)

 $Q(\alpha,c)$  is a measure for the change in reaction rate when a kinetic parameter is perturbed from  $\alpha_{0i} = \ln k_{0i}$  to  $\alpha_i = \ln k_i$ .

 $Q(\alpha,c)$  can be approximated by the quadratic expression

$$\mathbf{Q}(\alpha) = (\Delta \alpha)^{1} \mathbf{F}^{1} \mathbf{F}(\Delta \alpha) \tag{A5}$$

where  $Q(\alpha) \simeq Q(\alpha,c)$  in the neighborhood of  $\alpha_0$ . The rank order of the importance of the reactions and the interconnections of the reactions are revealed by performing eigenvalueeigenvector decomposition of the matrix  $\mathbf{F}^{\mathrm{T}}\mathbf{F}$ .

Equation A4 can be rewritten in canonical form by introducing a new set of parameters  $\Psi = \mathbf{U}^{T} \alpha$ , where  $\mathbf{U}^{T}$  is the matrix of normalized eigenvector  $\mathbf{u}_i$  of  $\mathbf{F}^{\mathrm{T}}\mathbf{F}$  such that  $\mathbf{u}_i^{\mathrm{T}}\mathbf{u}_i = 1$  (i = 1, 2, ..., p).

$$Q(\Psi) = \sum_{j=1}^{p} \lambda_j (\Delta \Psi_j)^2$$
 (A6)

The new set of parameters are called principal components.  $\Delta \Psi$ =  $\mathbf{U}^{\mathrm{T}}(\Delta \alpha)$ ;  $\lambda_1 > \lambda_2 > \dots > \lambda_p$  are the eigenvalues of  $\mathbf{F}^{\mathrm{T}}\mathbf{F}$ . When a parameter is perturbed along an eigenvector  $\mathbf{u}_i$  in the space of the transformed coordinates  $\Psi_j$ ,  $\Delta \Psi_j = 0$  for  $i \neq j$ .  $Q(\Psi) = \lambda_i (\Delta \Psi_i)^2$ , and therefore  $\lambda_i$  measures the significance of reactions that occur in the principal component  $\Psi_i$ . Those reactions that are characterized by large eigenvectors and at the same time also belong to a reaction group characterized with a large eigenvalue are identified as the most important reactions in a mechanism. In practice, threshold values of eigenvalue and eigenvector are chosen so that chemical reactions that belong to a reaction group characterized with a small eigenvalue or reactions that belong to a reaction group characterized by a large eigenvalue but correspond to an eigenvector below the threshold value are considered redundant.

Close examination of the elements of an eigenvector that belongs to a specific eigenvalue may reveal connections among the reactions. For example, fast equilibria can be readily identified by two large eigenvector elements of equal value but of opposite signs. This may also be applied to a situation where species i is produced by one or more reactions and removed quickly by another set of one or more reactions; i.e., species i is then in a pseudo-steady state. These reactions and species are usually redundant because they have no effect on the kinetic behaviors of other species in the system.

In eq A5, all of the chemical species have been considered. Therefore, the reduced reactions mechanism should reproduce the kinetic behaviors of all species. In some cases, however, one might be interested only in reproducing the kinetic behaviors of all major chemical species or the "observed species"; then the mechanism can be greatly simplified. This type of restricted principal component analysis can also be used to identify reactions critical to the formation of individual chemical species.

A FORTRAN program package called KINAL<sup>22</sup> was developed by Turanyi to perform principal component analysis on both concentration sensitivity and rate sensitivity matrices. This package was used extensively in our analysis of the mechanism in Table 1.

#### **References and Notes**

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