### Shock-Tube Kinetics Studies of Formaldehyde Oxidation Reactions Involving NO₂, NO, and N₂O With and Without O₂

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### Abstract (Continue on reverse side if necessary and identify by block number)
An investigation of the combustion chemistry of Solid propellants is summarized.
Shock-Tube Kinetics Studies of Formaldehyde Oxidation Reactions Involving NO$_2$, NO, and N$_2$O With and Without O$_2$

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I. Statement of Problem

The detailed combustion chemistry of solid propellants in use by the U.S. Army is not understood. Of particular interest are the chemistry of nitrocellulose as well as double base and nitramine propellants in general, and the gas-phase reactions of cyclotetramethylene-trinitramine (RDX) and of cyclotetramethylene tetranitramine (HMX) in particular. It appears\textsuperscript{1-3} that reactions between aldehyde and nitrogen dioxide, besides nitric oxide and nitrous oxide, dominate the gas-phase combustion processes near the propellant surface in these systems, and it is important to obtain a quantitative understanding of the overall kinetics for engineering applications and, in the long run, a detailed quantitative knowledge of the dominant reaction mechanisms and their relevant rate coefficient for future computer modeling of the gas-phase propellant chemistry.

Some shock-tube measurements of importance for these systems have been conducted in the past.\textsuperscript{1-3} However, they were based upon \textit{in situ} measurements of only one fuel-intermediate (CH\textsubscript{3}ONO\textsubscript{2} or CH\textsubscript{3}CH\textsubscript{2}ONO\textsubscript{2} in ref. 3) or only an oxidizer species (NO\textsubscript{2} in refs. 1
and 2 or N₂O in ref. 2), and product analysis was performed after quenching of the reacting mixture. Since shock-tube quenching methods usually cannot yield reliable information about the degree of reaction progress at a certain time after initiation, additional in situ shock-tube measurements were required, particularly for the fuel species besides intermediates and products. Specifically, the oxidation of formaldehyde by NO₂, besides NO or N₂O, are of importance in this respect.

Previous studies⁴ at relatively low temperature (390 < T/°K < 465) and at about 0.4 atm total pressure showed that the reaction in homogeneous and first order in both, the formaldehyde and the nitrogen dioxide concentration with an overall rate coefficient whose pre-exponential factor and whose apparent activation energy increased with increasing temperature. These studies were conducted in a static reactor and the pressure-increase was used as a measure of the reaction progress with the result

\[-(H₂CO)'' = -0.724(NO₂)' = \bar{k}(H₂CO)(NO₂) , \quad (1)\]

where \( \bar{k} = 1.26 \times 10^{10} \exp(-15,000/RT) \text{ cm}³/\text{mole-sec} \) for 391 < T/°K < 433 and \( \bar{k} = 10^{12} \exp(-29,000/RT) \text{ cm}³/\text{mole-sec} \) for 433 < T/°K < 465.

In subsequent shock-tube studies¹,² in argon-diluted mixtures of H₂CO and NO₂ at elevated temperatures and pressures, the reaction progress was monitored by spectral absorption of NO₂ in the visible and resulted in an overall rate law for NO₂-consumption of the approximate form¹
\[-(\text{NO}_2)^* = E_p \sqrt{(\text{H}_2\text{CO})(\text{M})} (\text{NO}_2) \tag{2}\]

with \(E_p = 1.26 \times 10^{13} \exp(-26,700/RT) \text{cm}^3/\text{mole-sec}\) for \(992 < T/\text{K} < 1828\) and \(7.3 < p/\text{atm} < 12.3\). Thus, the dependence on reactants as well as the overall rate-coefficient appeared to change with increasing temperature and pressure.

Consequently, we have conducted additional measurements behind reflected shock-waves for temperatures of \(835 < T/\text{K} < 1175\) and for total pressures of \(0.96 < p/\text{atm} < 2.85\) for varying initial concentrations of \(\text{H}_2\text{CO}\) and \(\text{NO}_2\) by using HeXe-laser absorption at 3.508\(\mu\) for monitoring \(\text{H}_2\text{CO}\) as well as infrared emission near 3.5\(\mu\) and near 7.5\(\mu\) for \(\text{H}_2\text{CO}\) and \(\text{NO}_2\).

In the following we summarize important results which were obtained during the last two years of this research effort, after redirection of our studies on the chemistry of combustion inhibition by \(\text{CF}_3\text{Br}\) after the first contract year.

II. Summary of Most Important Results

A. Overall Rate Parameters

We have obtained empirically overall induction (I), fast reaction (R), and equilibrium (E) times for our experimental conditions. The induction time \(I_I\) was defined by the time interval between the reflected-shock arrival at the laser observation-station and the intercept of the maximum slope for the HeXe-laser transmission rate with the initial transmission \(I_0\) after reflected shock-
heating. Our data could be fitted best by the relation

\[ \tau_1(H_2C)_0(NO_2)_0/(M)_0 = \frac{k^{-1}}{k_1} = \frac{(H_2CO)_0(NO_2)_0}{(H_2CO)} \]  

(3)

where

\[ k_1 = 3.03 \times 10^{17} (\pm 76\%) \exp[-29,100(\pm 5.2)/RT] \text{ cm}^3/\text{mole-sec} \]  

(3a)

is an effective rate-parameter, and the quality of the least-squares-fit is \( r^2 = 0.941 \). The initiation rate-parameter \( k_1 \) is approximately related to the rate-coefficient \( k_i \) for the initiation step of the \( H_2CO-NO_2 \)-reaction by

\[ k_i = F k_{1} = \frac{(\ln I_1/\ln I_0)}{(\ln I_\infty/\ln I_0)} \frac{(H_2CO)_0}{(M)_0} \]  

(3b)

where \( I_\infty = \) laser transmission after reaction completion, \( I_0 = \) initial laser transmission, and \( I_1 = \) laser transmission at \( t = \tau_1 \), where \( F = 10^{-2} \) (see below). The experimentally established relation (3) shows that the induction-rate is first-order in both, the initial \( H_2CO \)- and the initial \( NO_2 \)-concentration.

The equilibrium times \( \tau_E \) where defined by the time interval between the reflected-shock arrival at the laser observation-station and the intercept of the maximum slope for the HeXe-laser-transmission rate with the final transmission \( I_\infty \) after completion of the reaction.
The data could be fitted best by the relation

\[ \tau_E (H_2CO)_o (NO_2)_o / (M)_o = \frac{(H_2CO)_o (NO_2)_o}{(H_2CO)_E} \]

(4)

where

\[ \bar{k}_E = 2.03 \times 10^{16} (\pm 85\%) \exp[-22,800 (\pm 7.6%) / RT] \text{ cm}^3 / \text{mole-sec} \]  

(4a)

is the effective rate-parameter for reaching equilibrium with a least-squares-fit quality of \( r^2 = 0.892 \). The empirical result (4) shows that the overall rate for equilibration is also first order in both the initial \( H_2CO^- \) and the initial \( NO_2^- \)-concentration. Thus, it can be implied that the overall oxidation of \( H_2CO \) with \( NO_2 \) is first-order throughout in both \( (H_2CO) \) and \( (NO_2) \).

From the fit-data for \( \tau_I \) and \( \tau_E \) followed for the fast-reaction time \( \tau_R = \tau_E - \tau_R \)

\[ \tau_R (H_2CO)_o (NO_2)_o / (M)_o = \frac{(H_2CO)_o (NO_2)_o}{(H_2CO)_R} \]

(5)

where

\[ \bar{k}_R = 4.02 \times 10^{15} (\pm 13\%) \exp[-18,100 (\pm 1.6%) / RT] \text{ cm}^3 / \text{mole-sec} \]  

(5a)

is the effective rate-parameter for the rapid-reaction regime at constant pressure and the least-squares-fit quality is \( r^2 = 0.998 \). The rapid-rate parameter \( \bar{k}_R \) is approximately related to the overall rate-coefficient \( k_R \) for the maximum \( H_2CO \) consumption-rate by
with the same meaning of symbols as given under equation (3b) and 
Gr = 10^{-1} - 10^{-2} (see below).

From the results (3) through (5) follows that the consumption of \( \text{H}_2\text{CO} \) by oxidation with \( \text{NO}_2 \) is first-order in \( \text{H}_2\text{CO} \) and first-order in \( \text{NO}_2 \) as was also found in reference 4, but not by the observations in references 1 through 3. The apparent activation energy decreases from 29.1 kcal/mole during the induction regime to 18.1 kcal/mole during the fast oxidation regime. Here the activation energy for the rapid oxidation regime is similar to that (-19 kcal/mole) observed above 433\(^\circ\)K in reference 4, although the pre-exponential for the effective rate-coefficient \( k_R \) is larger than that for \( K \) by factors of 10-100.

B. Initiation Step

Rate data for the initiation step were obtained by measuring the early \( \text{H}_2\text{CO} \) consumption rate at the time of reaction-initiation immediately after shock-heating. The HeXe-laser transmission exhibited a finite initial rate in all cases. Analysis of the rates in terms of the initial rates for \( \text{H}_2\text{CO} \) resulted in

\[-(\text{H}_2\text{CO})' = k_1(\text{H}_2\text{CO})(\text{NO}_2) \, . \]
Here,

\[
k_{1} = (M)_{0}^{-1}(\text{NO}_{2})_{0}^{-1} \left[ \frac{(\ln I_{t}/I_{\infty})}{(\ln I_{I}/I_{\infty})} \right]_{t=0}
\]

\[
= 3.46 \times 10^{16} (\pm 102\%) \exp[-29,600(\pm 7.1\%)/RT] \text{ cm}^{3}/\text{mole-sec} \quad (6a)
\]

is the rate-coefficient for the initiation-step from a least-squares-fit with a quality of \( r^2 = 0.970 \).

The result demonstrates that the initiation-step is first-order in both the \( \text{H}_{2}\text{CO} \)- and the \( \text{NO}_{2} \)-concentration, as expected from the relation (3) above, and it confirms that \( F = 10^{-2} \) in equation (3b). Within the experimental errors, the activation energy \( E_{1} \) for the initiation-step (6) is the same as the effective activation energy \( E_{I} \) for the induction-regime (3a).

The relatively large pre-exponential factor and low activation energy for \( k_{1} \) can be rationalized by invoking unimolecular rate theory in the high pressure limit for the formation of a vibrationally excited complex \( Q^{*} \equiv (\text{NO}_{2} \cdot \text{H}_{2}\text{CO}) \) which is subsequently decomposed by collisions with a third body (M) to products \( R_{1} \) and \( R_{2} \) according to

\[
\text{H}_{2}\text{CO} + \text{NO}_{2} \rightarrow Q^{*} , \quad (i)
\]

\[
Q^{*} + M \rightarrow R_{1} + R_{2} + M . \quad (d)
\]

Here, some or all of the products can react further with \( \text{H}_{2}\text{CO} \) and
NO$_2$ by chain and/or regular reactions. For ($Q^*$) in a steady state and $k_d(M) \gg k_{-1}$ follows the initiation-step (6). The rate-coefficient $k_i$ can be obtained from a "primitive" unimolecular theory, viz.,

$$k_i = 10^{13} e^{E_1/RT} \frac{(E_1/RT)^{f-1}}{(f-1)!}$$

which satisfies (6a) with a reasonable number of vibrational degrees of $f = 5-6$ excited in $Q^*$ and a reasonable decay time of $\tau_{-1} = k_{-1}^{-1} = 10^{-13}$ sec for $Q^*$. It is interesting to note that this expression extrapolates within the experimental uncertainties to the values of $k$ obtained for the slow initial reaction at lower temperatures in reference 4. Thus, it appears that the same initiation step applies at low and at elevated temperatures.

C. Fast Oxidation Regime

Rate data for the rapid oxidation regime were obtained by determining $k_R$ directly from the relation [comp. (5b)]

$$k_R = \frac{(I_o - I_0)}{I_m(\ln I_m/I_0)(NO_2)_o \tau_R} \quad (\approx Gr E_R)$$

which applies for the maximum rate of H$_2$CO-consumption with $I_m$ the HeXe-laser transmission at the time of maximum H$_2$CO-consumption. A least-squares-fit to the data results in

$$R = 7.85 \times 10^{13} (\pm 122\%) \exp[-16,000 (\pm 14.7\%)/RT] \text{cm}^3/\text{mole-sec} \quad (7b)$$
with a quality of $r^2 = 0.780$. The activation energy for $k_R$ is, within the experimental uncertainties, the same as that determined for $k_R$ in equation (5a), and the expression (7b) confirms $Gr = 10^{-1} - 10^2$ in the relation (5b). The pre-exponential factor of $\sim 10^{14}$ cm$^3$/mole-sec in (7b) is reasonable for a binary reaction rate-coefficient.

It should be noted that, within the error limits, $E_R = E_i/2$ which implies a short chain mechanism for the rapid reaction regime with chain branching and chain propagation steps of low or negligible activation energies and with a bimolecular chain-termination step involving two chain carriers. Since $k_R$ was determined with $T$ taken as the temperature at the initiation of the reaction, and since $T$ increases during the course of the oxidation process by potentially highly exothermic reactions, the heat-release will influence the maximum oxidation-rate and the value for $E_R$ above is a lower limit for the actual overall rate coefficient for the maximum oxidation rate. However, this effect is small in view of the dilution of the system with total reactant concentration of $\leq 15\%$, and amounts to less ($\leq 12\%$) than the experimental error in $E_R$.

Elucidation of the detailed reaction mechanism requires further study, particularly in view of the differences in the reactant orders for the overall oxidation process obtained by us as opposed to those in references 1 through 3 and because of our confirmation of its first order.
D. Additional Results

We have obtained evidence for the existence of a formaldehyde dimer in the gas-phase at room temperatures and at high temperatures after shock-heating in pure and argon-diluted mixtures of formaldehyde. The line-strengths for the monomer \( (m) \) and dimer \( (d) \) of \( \text{H}_2\text{CO} \) near the HeXe-laser wavelength of \( \lambda_L = 3.508 \mu \) as a function of temperature are (in \( \text{cm}^{-2} \text{-atm}^{-1} \)) for \( 285 < T/\text{OK} < 1600 \), respectively,

\[
S_m(T) = S_0^m(T_0/T)^m
\]

with \( m = 1.94 (\pm 7.3\%) \) and

\[
S_d(T) = (SK/b)_d^0(T/T_0)^{n+\frac{1}{2}} \exp\left\{ +\left( \frac{\Delta H_0}{RT_0} \right) \left( \frac{T_0}{T} - 1 \right) \right\}
\]

with \( n = 1.07(\pm 37\%) \), \( (SK/b)_d^0 = 3.67 (\pm 0.7\%) \text{ cm}^{-1}\text{-atm}^{-1} \), and \( \Delta H_0 = 940 \text{ cal/mole} \) a theoretical estimate for the heat of formation for the dimer species.

HeXe-laser absorption by argon-diluted \( \text{NO}_2 \) at 3.508\( \mu \) at room-temperatures and elevated temperatures revealed no dependence on total pressure and can be expressed for \( 285 < T/\text{OK} < 2000 \) by an absorption coefficient (in \( \text{cm}^{-1}\text{-atm}^{-1} \)) of the form

\[
P(T) = A(T_0/T)^{m+\frac{1}{2}} \exp\left\{ -(E_0/RT_0) \left( \frac{T_0}{T} - 1 \right) \right\} \times \left[ 1 - \exp(-h c w_L/k T) \right],
\]

where \( A = 1.37 \times 10^{-2} \text{ cm}^{-1}\text{-atm}^{-1} \), \( m = 2.54 \), and \( E_0 = 5.66 \text{ kcal/mole} \)
with a least-squares-fit quality of $r^2 = 0.885$.

Approximate analytical relations for the spectral intensity distribution and the radiative recombination rate-coefficient for Br-atom free-bound transitions have been derived\(^9\) for Br-atom concentration measurements in the context of initial studies on the chemistry of combustion inhibition by CF\(_3\)Br before re-direction of the impphasis of our research towards H\(_2\)CO-oxidation. In addition, a simple method for calculating Voigt-profiles by a programmable hand-calculator (HP-34C) was developed\(^10\) which is useful for laser-absorption studies on gases.

III. List of Publication


IV. List of Participating Scientific Personnel

1. Dr. Klaus G. P. Sulzmann, Principal Investigator;
2. Dr. Chang Tang;
3. Mr. Muhittin Akyuz;
4. Mr. Daniel Baxter, B.A., Spring 1983;
5. Mr. Anthony Hamins; M.S., Fall 1982
6. Mr. Paul Hannan;
7. Mr. Thomas S. Lund, B.A., Spring 1983;
8. Ms. Shoou Shiah;
9. Mr. Lam Tran;
10. Mr. Robert Wallach.
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IV. References


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