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SHOCK-TUBE KINETICS STUDIES OF FORMALDEHYDE OXIDATION
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JOLLA K G SULZMANN 04 MAY 83 ARD-16791.5-EG
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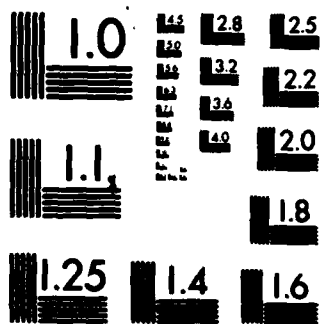
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FINAL REPORT

USARO Contract No. DAAG29-80-C-0001

January 1, 1980 through February 28, 1983

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

Submitted by

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Shock-Tube Kinetics Studies of Formaldehyde
Oxidation Reactions Involving NO_2 , NO , and
 N_2O 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 appears¹⁻³ 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.¹⁻³ However, they were based upon in situ measurements of only one fuel-intermediate (CH_3ONO_2 or $\text{CH}_3\text{CH}_2\text{NO}_2$ in ref. 3) or only an oxidizer species (NO_2 in refs. 1

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and 2 or N_2O 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 NO_2 , besides NO or N_2O , are of importance in this respect.

Previous studies⁴ at relatively low temperature ($390 \leq T/^{\circ}\text{K} \leq 465$) 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

$$-(\text{H}_2\text{CO})' = -0.724(\text{NO}_2)' = \bar{k}(\text{H}_2\text{CO})(\text{NO}_2), \quad (1)$$

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

In subsequent shock-tube studies^{1,2} in argon-diluted mixtures of H_2CO and NO_2 at elevated temperatures and pressures, the reaction progress was monitored by spectral absorption of NO_2 in the visible and resulted in an overall rate law for NO_2 -consumption of the approximate form¹

$$-(\text{NO}_2)^{\circ} = k_F \sqrt{(\text{H}_2\text{CO})(\text{M})} (\text{NO}_2) \quad (2)$$

with $k_F = 1.26 \times 10^{13} \exp(-26,700/RT) \text{ cm}^3/\text{mole-sec}$ for $992 \leq T/^{\circ}\text{K} \leq 1828$ and $7.3 \leq p/\text{atm} \leq 12.3$. 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 $835 \leq T/^{\circ}\text{K} \leq 1175$ and for total pressures of $0.96 \leq p/\text{atm} \leq 2.85$ for varying initial concentrations of H_2CO and NO_2 by using HeXe-laser absorption at 3.508μ for monitoring H_2CO as well as infrared emission near 3.5μ and near 7.5μ for H_2CO and 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 CF_3Br 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 τ_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

$$\tau_I (\text{H}_2\text{C})_0 (\text{NO}_2)_0 / (\text{M})_0 \equiv \bar{k}_I^{-1} = \frac{(\text{H}_2\text{CO})_0 (\text{NO}_2)_0}{(\text{H}_2\text{CO})_I^*}, \quad (3)$$

where

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

is an effective rate-parameter, and the quality of the least-squares-fit is $r^2 = 0.941$. The initiation rate-parameter $\bar{k}_I$ is approximately related to the rate-coefficient k_i for the initiation step of the $\text{H}_2\text{CO}-\text{NO}_2$ -reaction by

$$k_i = F\bar{k}_I = \frac{(\ln I_I/I_0)}{(\ln I_\infty/I_0)} \frac{(\text{H}_2\text{CO})_0}{(\text{M})_0}, \quad (3b)$$

where I_∞ = laser transmission after reaction completion, I_0 = initial laser transmission, and I_I = laser transmission at $t = \tau_I$, 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 τ_E were 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_∞ after completion of the reaction.

The data could be fitted best by the relation

$$\tau_E (\text{H}_2\text{CO})_O (\text{NO}_2)_O / (M)_O \equiv \bar{k}_E^{-1} = \frac{(\text{H}_2\text{CO})_O (\text{NO}_2)_O}{(\text{H}_2\text{CO})_E} \quad (4)$$

where

$$\bar{k}_E = 2.03 \times 10^{16} (\pm 85\%) \exp[-22,800 (\pm 7.6\%) / RT] \text{ cm}^3/\text{mole-sec} \quad (4a)$$

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 τ_I and τ_E followed for the fast-reaction time $\tau_R (= \tau_E - \tau_I)$

$$\tau_R (\text{H}_2\text{CO})_O (\text{NO}_2)_O / (M)_O \equiv \frac{(\text{H}_2\text{CO})_O (\text{NO}_2)_O}{(\text{H}_2\text{CO})_R} \quad (5)$$

where

$$\bar{k}_R = 4.02 \times 10^{15} (\pm 13\%) \exp[-18,100 (\pm 1.6\%) / RT] \text{ cm}^3/\text{mole-sec} \quad (5a)$$

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

$$k_R \approx \bar{k}_R Gr \approx 2 \frac{(I_\infty - I_0)}{(I_\infty + I_0)} \frac{(H_2CO)_0 / (M)_0}{(\ln I_\infty / I_0)} \bar{k}_R \quad (5b)$$

with the same meaning of symbols as given under equation (3b) and $Gr \approx 10^{-1} - 10^{-2}$ (see below).

From the results (3) through (5) follows that the consumption of H_2CO by oxidation with NO_2 is first-order in H_2CO and first-order in 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°K in reference 4, although the pre-exponential for the effective rate-coefficient k_R is larger than that for $\bar{k}$ by factors of 10-100.

B. Initiation Step

Rate data for the initiation step were obtained by measuring the early H_2CO 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 H_2CO resulted in

$$-(H_2CO)' = k_1 (H_2CO)(NO_2) \quad (6)$$

Here,

$$k_1 = (M)_0^{-1} (NO_2)_0^{-1} \left[\frac{(\ln I_t / I_\infty)}{(\ln I_L / I_\infty) t} \right]_{t \rightarrow 0}$$

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

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

The result demonstrated that the initiation-step is first-order in both the H_2CO - and the NO_2 -concentration, as expected from the relation (3) above, and it confirms that $F \approx 10^{-2}$ in equation (3b). Within the experimental errors, the activation energy E_i 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 theory⁵ in the high pressure limit for the formation of a vibrationally excited complex $Q^* \equiv (NO_2 \cdot H_2CO)$ which is subsequently decomposed by collisions with a third body (M) to products R_1 and R_2 according to



Here, some or all of the products can react further with H_2CO 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,⁵ viz.,

$$k_i \approx 10^{13} e^{-E_i/RT} \frac{(E_i/RT)^{f-1}}{(f-1)!} \quad (6b)$$

which satisfies (6a) with a reasonable number of vibrational degrees of $f \approx 5-6$ excited in Q^* and a reasonable decay time of $\tau_{-1} = k_{-1}^{-1} \approx 10^{-13}$ sec for Q^* . It is interesting to note that this expression extrapolates within the experimental uncertainties to the values of $\bar{k}$ 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)]

$$k_R = \frac{(I_\infty - I_0)}{I_m (\ln I_\infty / I_0) (\text{NO}_2)_0 \tau_R} \quad (= \text{Gr } \bar{k}_R) \quad (7)$$

which applies for the maximum rate of H_2CO -consumption with I_m the HeXe-laser transmission at the time of maximum H_2CO -consumption. A least-squares-fit to the data results in

$$k_R = 7.85 \times 10^{13} (\pm 122\%) \exp[-16,000 (\pm 14.7\%)/RT] \text{ cm}^3/\text{mole-sec} \quad (7b)$$

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 $Gr \approx 10^{-1} - 10^2$ in the relation (5b). The pre-exponential factor of $\sim 10^{14}$ cm³/mole-sec in (7b) is reasonable for a binary reaction rate-coefficient. It should be noted that, within the error limits, $E_R \approx E_i/2$ 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.⁶ The line-strengths for the monomer (m) and dimer (d) of H_2CO 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 $285 \leq T/^{\circ}\text{K} \leq 1600$, respectively,

$$S_m(T) = S_m^0(T_0/T)^m \quad (8)$$

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

$$S_d(T) = (SK/b)_d^0 (T/T_0)^{n+\frac{1}{2}} \exp[+(\Delta H_0/RT_0)(T_0/T-1)] \quad (9)$$

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 estimate⁷ for the heat of formation for the dimer species.

HeXe-laser absorption by argon-diluted NO_2 at 3.508μ at room-temperatures and elevated temperatures revealed no dependence on total pressure and can be expressed for $285 \leq T/^{\circ}\text{K} \leq 2000$ by an absorption coefficient (in $\text{cm}^{-1}\text{-atm}^{-1}$) of the form⁸

$$P(T) = A(T_0/T)^{m+\frac{1}{2}} \{ \exp[-(E_0/RT_0)(T_0/T-1)] \} \times [1 - \exp(-hcw_L/kT)] , \quad (10)$$

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 derived⁹ for Br-atom concentration measurements in the context of initial studies on the chemistry of combustion inhibition by CF_3Br before re-direction of the emphasis of our research towards H_2CO -oxidation. In addition, a simple method for calculating Voigt-profiles by a programmable hand-calculator (HP-34C) was developed¹⁰ which is useful for laser-absorption studies on gases.

III. List of Publication

1. "Approximate Analytical Relations for Radiative Recombination of Br-Atoms by Free-Bound Transitions," K. G. P. Sulzmann and A. Hamins, J. Quant. Spectry. and Rad. Transf. 26, 307 (1981).
2. "3.508 μ -HeXe-Laser Absorption by Formaldehyde Monomer and Dimer and by Nitrogen Dioxide Monomer and Dimer Without and in the Presence of Argon," K. G. P. Sulzmann, A. Hamins, and S. Y. Tang, J. Quant. Spectry. and Rad. Transf. 29, 31 (1983).
3. "A Simple Method for Calculating Voigt Profiles by a Programmable HP-34 Hand Calculator," K. G. P. Sulzmann, J. Quant. Spectry. and Rad. Transf. 29, 89 (1983).

IV. List of Participating Scientific Personnel

1. Dr. Klaus G. P. Sulzmann, Principal Investigator;
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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;
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10. Mr. Robert Wallach.

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9. K. G. P. Sulzmann and A. Hamins, JQSRT 26, 307 (1981).
10. K. G. P. Sulzmann, JQSRT 29, 89 (1983).

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