CLOSE-OUT REPORT

to

Fundamental Interaction Branch

Chemical Sciences Division

Office of Energy Research

U. S. Department of Energy

"Kinetics and Mechanisms of Key

Elementary Processes of Importance to

High Temperature Combustion Chemistry"

DOE contract NO: DE-FG05-85ER13373

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(with extension to 8-31-89)

MASTER

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Summary

In the project funded by DOE under contract number DE-FG05-85ER13373 for the period of June 1, 1985 - May 31, 1987 with approved extension to August 31, 1989, we have investigated the kinetics and mechanisms numerous reactions involving many key reactive combustion species: CH_2O, CH_3O, CH, NO, NO_2, CH_3OH, C_2H_5OH, i-C_3H_7OH, t-C_4H_9OH, C_6H_5, C_6H_5O and C_6H_6, among others. A total of 24 reactive systems have been studied, resulting in 10 published papers; 1 in press; 2 submitted; 4 under preparation; 8 under analysis, and 8 technical presentations.

I. INTRODUCTION

In this collaborative study between the Catholic University of America and Naval Research Laboratory covering the period of June 1, 1985 and May 31, 1987, with extension to August 31, 1989, we have employed three different techniques to investigate the kinetics and mechanisms of several important reactions of importance to combustion chemistry. In the first method, we employed a static pyrolytic system to study the kinetics of reactions of CH_3O, a very important hydrocarbon oxidation intermediate. The reactions studied include $CH_3O + NO_x$ and the unimolecular decomposition reaction, for which we have obtained the first set of kinetic data. In the second method, we employed the high temperature shock tube facility at NRL to elucidate the mechanisms of benzene oxidation and alcohol decomposition and oxidation chemistry. Very important data have been obtained for CH_3OH, C_2H_5OH, i-C_3H_7OH and t-C_4H_9OH decomposition reactions. In the third method we utilized the two-laser pump-probe technique to study the kinetics of CH reactions with N_2O, SO_2, COS and CS_2. These processes are important to combustion chemistry of coal and shale oil derivatives.

A total of 24 reactive systems have been investigated with 10 papers published, 1 in press, 2 submitted, 4 in preparation, and 8 under analysis; 8 presentations have been made. Key processes studied are briefly described below.

II. ACCOMPLISHMENTS

A. Kinetics of CH_3O radical reactions

CH_3O is one of the most important hydrocarbon combustion species whose reaction rates have not yet been reliably measured. We have recently studied its

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reaction with NO and HNO and its unimolecular decomposition reaction by pyrolyzing CH_3ONO in a static cell (440 - 530 K) and in a shock tube (1100 - 1600 K).

In the static cell study, the reactant and products (NO, CH_2O, N_2O, CO and CH_3OH) were analyzed by FTIR. Kinetic modeling of the decay of CH_3ONO and the formation of these various products, aided by the RRKM theory, yielded several key rate constants for T = 440-530 K and P = 710 torr of He:

$$CH_3ONO \rightarrow CH_3 + NO \qquad\qquad (1)$$

$$k_1(710 \text{ torr}) = 10^{15.30\pm030} \exp (-38,700 \pm 400/RT) \text{ sec}^{-1}$$

$$k_1 (\infty) = 10^{16.0\pm0.3} \exp (-39,600 \pm 400/RT) \text{ sec}^{-1}$$

$$CH_3O + NO \rightarrow CH_3ONO \qquad\qquad (2)$$

$$k_2(710 \text{ torr}) = 10^{12.96\pm0.30} \text{ cc/mole·sec}$$

$$CH_3O + NO \rightarrow CH_2O + HNO \qquad\qquad (3)$$

$$k_3(710 \text{ torr}) = 10^{13.5\pm0.4} \exp (-2050 \pm 200/RT) \text{ cc/mole·sec}$$

$$CH_3O + HNO \rightarrow CH_3OH + NO \qquad\qquad (4)$$

$$k_4 = 10^{13.5\pm0.4} \exp (0 \pm 400/RT) \text{ cc/mole·sec}$$

$$HNO + HNO \rightarrow N_2O + H_2O$$
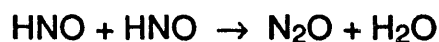
$$k_5 = 10^{8.93\pm0.30} \exp (-3100 \pm 300/RT) \text{ cc/mole·sec}$$

Reactions (1) - (3) were found to be pressure and/or temperature dependent over a broad range of conditions. These dependencies are believed to be the main cause of large discrepancies in many reported k_3/k_2 values. Reaction (5), which is a process of much uncertainty and controversy over the years, could be quantitatively accounted for

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by the TST - RRKM theory using the TST-parameters recently obtained by C. Melius for the rate-controlling step involved in the initial H-migration:

$$2HNO \leftrightarrow \left[\begin{array}{c} H-N=O \\ | \\ O=N-H \end{array} \right]^{\ddagger} \rightarrow \begin{array}{c} H \quad OH \\ \backslash \diagup \\ N \\ | \\ O=N \end{array} \rightarrow\rightarrow N_2O + H_2O$$
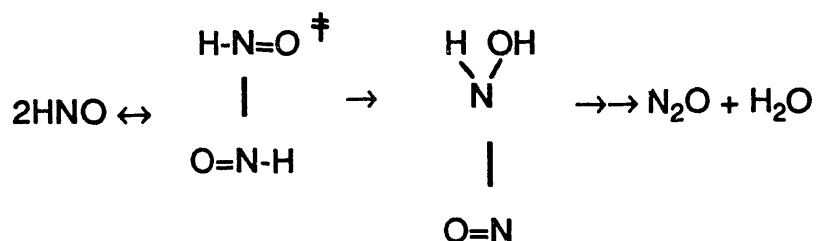
The results of Melius' BAC-MP4 calculations indicate that more than half a dozen stable intermediates may be involved in this interesting reaction.

In our shock tube study of the CH_3ONO decomposition above 1100 K, we measured time-resolved yields of CO which were found to depend quite sensitively on the rate of the CH_3O decomposition reaction:

$$CH_3O + M \rightarrow CH_2O + H + M \qquad\qquad (6)$$

Kinetic modeling of CO production at 1100 - 1600 K (shock tube) and at 550 - 730 K (static cell) using the key rate constants established above gave rise to the second-order rate constant (with Ar or He as a diluent):

$$k_6 = (5.45\pm0.63) \times 10^{13} \exp(-6794 \pm 102/T) \text{ cc/mole·sec}$$

This result differs significantly from that recommended by Tsang and Hampson (J. Phys. Chem. Ref. Data 15, 1087 (1986)). Recently M. Page at NRL has carried out an extensive ab initio calculation for the $CH_3O \leftrightarrow CH_3O^{\dagger} \leftrightarrow CH_2O + H$ system and obtained the energy barriers for the forward and reverse reactions, $E^{\circ}_6 = 25.6$ and $E^{\circ}_{-6} = 8.0$ kcal/mole. respectively. The relatively large reverse barrier suggests that H-

tunneling may play a role in the decomposition process. On the basis of the calculated structures, vibrational frequencies and energy barriers, we carried out an RRKM calculation with and without tunneling. It is seen that the observed values are consistent with the energy barrier $E°_6 = 25.6$ kcal/mole with tunneling correction. Our data represent the first set of experimental values for the CH_3O decomposition reaction.

B. Reactions of CH_2O with H and CH_3.

CH_2O is a very important hydrocarbon combustion intermediate. It can be formed by the oxidation of various hydrocarbon radicals. The most important process is the oxidation of CH_3, which is usually the most stable and abundant alkyl radical, by O, OH, O_2 and HO_2. Accordingly, the reactions of CH_2O with H, O, OH and CH_3 are quite important in hydrocarbon combustion chemistry.

For the reaction,

$$H + CH_2O \rightarrow CHO + H_2, \tag{7}$$

different mixtures of CH_3ONO and 1,3,5-trioxane, $(CH_2O)_3$, the sources of H and CH_2O, respectively, were pyrolyzed in the shock tube. Kinetic modeling of CO production profiles at temperatures between 1150 and 1700 K gave rise to

$$k_7 = 10^{13.63 \pm 0.09} \exp (-2680 \pm 310/T) \text{ cc/mole·sec}$$

combination of our high temperature data with low temperature values led to

$$k_7 = 7.6 \times 10^7 T^{1.66} \exp (-1000/T) \text{ cc/mole·sec}$$

covering 260 - 1700 K. Our high temperature values are in good accord with other data, particularly the lower temperature ones.

In our study of the $CH_3 + CH_2O$ reaction,

$$CH_3 + CH_2O \rightarrow CH_4 + CHO \qquad (8)$$

we employed a mixture of di-t-butyl peroxide (a convenient source of CH_3) and $(CH_2O)_3$, highly diluted in Ar. Kinetic modeling of measured CO production profiles covering 1170 - 1630 K led to

$$k_8 = 10^{15.0\pm0.4} \exp(-11,600\pm1260/T) \text{ cc/mole·sec}$$

A nonlinear least-squares analysis of these high temperature data with those measured at lower temperatures gave

$$k_8 = 10^{-12.05} T^{7.4} \exp(483/T) \text{ cc/mole·sec}$$

The result of a TST-calculation indicates that our high temperature data are much larger than the calculated values and the deviation could be attributed to the H-tunneling effect.

C. Kinetics and mechanism of the $H + CH_3OH$ reaction

The reaction of H atoms with CH_3OH is a key process in CH_3OH decomposition and oxidation reactions. CH_3OH is an important alternate fuel which can be synthesized from syngas. Several reaction paths have been suggested previously for $H + CH_3OH$:

$$H + CH_3OH \rightarrow CH_2OH + H_2 \qquad\qquad (9a)$$

$$\rightarrow CH_3O + H_2 \qquad\qquad (9b)$$

$$\rightarrow CH_3 + H_2O \qquad\qquad (9c)$$

The most controversial one given above is (9c), which generates CH_3 as a chain-carrier instead of H atoms which can be produced from (9a) and (9b) due to the rapid decomposition of CH_2OH and CH_3O. Westbrook and Dryer (Combust. Sci. Techn. 20, 125 (1979)) adopted Aders and Wagner's earlier data on (9c) to model CH_3OH oxidation chemistry and concluded it to be important. But the validity of (9c) has been questioned and negated by Wagner and coworkers (18th Symp. (Int.) on Combust., p 831, 1981) in their subsequent, more detailed study.

In order to elucidate the mechanism of this important process, we have recently modeled experimentally measured H-atom decay rates by several laboratories using the discharge flow method based on our calculated rate constants for the following reactions according to the RRKM theory:

$$H + CH_2OH \rightarrow CH_3OH^* \rightarrow CH_3 + OH$$
$$CH_2OH + CH_2OH \rightarrow (CH_2OH)_2^* \rightarrow H_2O + CH_2 = CHOH$$

The results of this detailed modeling effort reveals that the key reactions leading to H_2O (which was the basis of the original assumption for (9c)) are:
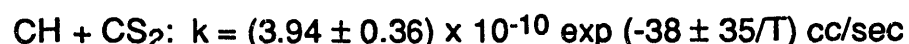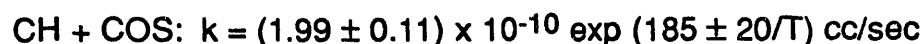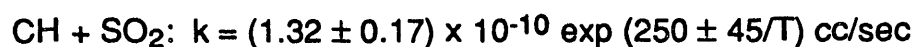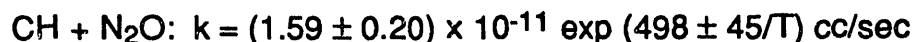
$$H + CH_2OH \rightarrow CH_3 + OH$$
$$OH + CH_3OH \rightarrow H_2O + CH_2OH$$
$$OH + CH_2O \rightarrow H_2O + CH_2OH$$
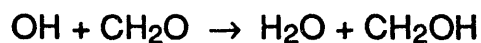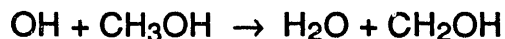
A least-squares analysis of these remodeled data led to

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$$k_{9a} = 3.2 \times 10^8 \, T^{1.49} \, \exp(-2140/T) \text{ cc/mole·sec}$$

covering the temperature range of 295 - 2100 K.

D. Kinetics of the reactions of CH radicals with N_2O, SO_2, COS and CS_2

      A series of experiments has been performed recently on the reactions of CH with N_2O, SO_2, COS and CS_2 using the technique of LIF. The rate constants measured in the temperature range of 300 - 670 K are given as follows.

$$CH + N_2O: \ k = (1.59 \pm 0.20) \times 10^{-11} \, \exp(498 \pm 45/T) \text{ cc/sec}$$

$$CH + SO_2: \ k = (1.32 \pm 0.17) \times 10^{-10} \, \exp(250 \pm 45/T) \text{ cc/sec}$$

$$CH + COS: \ k = (1.99 \pm 0.11) \times 10^{-10} \, \exp(185 \pm 20/T) \text{ cc/sec}$$

$$CH + CS_2: \ k = (3.94 \pm 0.36) \times 10^{-10} \, \exp(-38 \pm 35/T) \text{ cc/sec}$$

These data may be relevant to NO/N_2O hydrocarbon flame chemistry and sulfur-containing fuel chemistry.

      The inspection of these data reveals no correlation with the strength of the bonds involved, quite similar to that observed for the CH + alkane reactions in which no preference for primary, secondary or tertiary C-H bonds was noted. Interestingly, the rate of the CH reaction with SF_6, which has been used commonly as a diluent, was found to be too slow to measure.

E. Kinetics and mechanism of the $CH_2 + N_2$ reaction

      To understand the mechanism of the $CH_2 + N_2$ reaction, which has been considered as a possible prompt NO precursor reaction, we have carried out RRKM calculations on the reaction and also examined the possible contribution from the excited $^1CH_2$ species at high temperatures. The result of these calculations indicates

that the $CH_2 + N_2 \rightarrow HCN + NH$ process is too slow to compete with the $CH + N_2$ reaction. Additionally, since the rate-controlling step lies int he exit product channel (forming $HCN + HH$), the 9 kcal/mole electronic energy carried by $^1CH_2$ has no effect on these product formation.

F. Kinetics and mechanism of C_6H_6 oxidation and related reactions

The oxidation and formation of C_6H_6 is very important to alternate fuel (derived from coal and shale oil) chemistry and soot formation processes involved in all hydrocarbon combustion systems. In order to unravel the complex oxidation mechanism of C_6H_6 at high temperatures, we have investigated the reactions of C_6H_5 and C_6H_5O radicals in shock waves by simultaneously monitoring the evolution of CO and H_2O using two CW CO lasers operating at different transitions. CO is an early and direct product of the C_6H_5O decomposition reaction:

$$C_6H_5O \rightarrow CO + C_5H_5 \tag{10}$$

We have earlier determined the rate constant of this unimolecular decomposition reaction using anisole as the radical source. Thus, the rate of CO production can provide a reliable measure for the oxidation of C_6H_5 by different oxidants such as O_2 and NO_2:

$$C_6H_5 + O_2 \leftrightarrow C_6H_5O_2 \rightarrow C_6H_5O + O \tag{11}$$

$$C_6H_5 + NO_2 \rightarrow C_6H_5O + NO \tag{12}$$
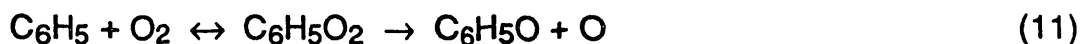
Both reactions have been studied. The former is a key chain initiation step in the C_6H_6 oxidation reaction, while the latter employed as an alternate chemical source of the C_6H_5O radical. Preliminary kinetic modeling of the observed CO production profiles led to

$$k_{11} = 10^{12.3} \exp(-3800/T) \text{ cc/mole·sec}$$

$$k_{12} = 10^{11} - 10^{12} \text{ cc/mole·sec}$$

at temperatures between 1150 and 1600 K based on the assumed C_6H_5 recombination rate, 3×10^{12} cc/mole·sec. Our k_{11} value at 773 K is about 10 times smaller than that estimated by Baldwin et al. (21st Symp. (Int.) on Combust. p. 991 (1986)). Since both k_{11} and k_{12} were found to be quite sensitive to the C_6H_5 recombination rate because of the high initial concentration of the radical generated by incident shock waves, a more detailed modeling of these two reaction systems should be delayed until a directly measured value for the recombination reaction is available.

G. Kinetics and mechanisms of the decomposition and oxidation of small alcohol molecules

A series of experiments has been carried out recently on the oxidation and/or decomposition of CH_3OH, C_2H_5OH, iso-C_3H_7OH and t-C_4H_9OH above 1200 K. Both CO and H_2O products were simultaneously probed as above. The objectives of these experiments lie in the identification of the rate-controlling steps for production of CO and H_2O in the presence and absence of O_2. In these systems, H_2O can be directly produced in the absence of O_2 either by OH abstraction reactions or direct molecular elimination reactions (for C_2, C_3 and C_4 alcohols). With the exception of the t-C_4H_9OH system, analysis of time-resolved product formation profiles are currently still under way and kinetically modeled results will be reported to DOE in a future date.

The t-C_4H_9OH molecule, which has been employed as a gasoline fuel additive, can occur by the following two-channels:

$$\text{t-}C_4H_9OH \rightarrow H_2O + \text{iso-}C_4H_8 \tag{13}$$

$$\rightarrow CH_3 + (CH_3)_2 COH \tag{14}$$

from kinetic modeling of H_2O and CO, which is formed mainly from the products of reaction (14), we obtained

$$k_{13} = 10^{14.50\pm0.30} \exp{(-32,900 \pm 900/T)} \ s^{-1}$$

$$k_{14} = 10^{16.48\pm0.24} \exp{(-40,900 \pm 700/T)} \ s^{-1}$$

for $1220 \leq T \leq 1620$ K. Our Arrhenius parameters for k_{13} are in excellent agreement with those reported by Lewis et al. (J. Am. Chem. Soc. 96, 4398 (1974)), while those for k_{14}, are in close agreement with the values calculated by Tsang (Int. J. Chem. Kinet. 16, 1543)).

III. Publications

1.   C.-Y. Lin and M. C. Lin, "The Combination Reaction of CH_3 and C_6H_5O", Aust. J. Chem. 39, 723 (1986).

2.   W. A. Sanders, C.-Y. Lin and M. C. Lin, "On the importance of the $CH_2 + N_2 \rightarrow HCN + NH$ as a precursor for prompt NO Formation", Combust. Sci, and Tech. 51, 103 (1987).

3.   W. A. Sanders and M. C. Lin, "Kinetics and mechanism of reactions of NF_2 with olefins: reinterpretation of existing data and estimation of C-N bond energies of alkyldifluoramines", JCS Faraday Trans. 2, 83, 905 (1987).

4.   W. A. Sanders and M. C. Lin, "Kinetics and mechanisms of methylidyne radical reactions", in Chemical Kinetics of Small Organic Radicals, vol III, Z. B. Alfasai, ed., p. 103, CRC Press, Boca Raton, Florida, 1988.

5.   Y. He, W. A. Sanders and M. C. Lin, "The thermal decomposition of methyl nitrite: Kinetic modeling of detailed product measurements by GLC and FTIR", J. Phys. Chem. 92, 5474 (1988).

6.   S. Zabarnick, J. W. Fleming and M. C. Lin, "Kinetics of CH radical reactions with N_2O, SO_2, COS, CS_2 and SF_6", Int. J. Chem. Kinet., 21, 765 (1989).

7.   T. K. Choudhury, W. A. Sanders and M. C. Lin, "Kinetic modeling of reactions of methyl radicals with formaldehyde and isobutane studied by molecular modulation spectroscopy", J. C. S. Faraday Trans. 2, 85, 801 (1989).

8.   T. K. Choudhury, W. A. Sanders and M. C. Lin, "A shock tube and modeling study of the $CH_3 + CH_2O$ reaction at high temperatures", J. Phys. Chem., 93, 5143 (1989).

9.   M. Page, M. C. Lin, Y. He and T. K. Choudhury, "Kinetics of the unimolecular decomposition of CH_3O: Theory and Experiment" J. Phys. Chem. 93, 4404 (1989).

10.   T. K. Choudhury and M. C. Lin, "Kinetics of the H + CH_2O reaction at high temperatures", Combust. Sci. Technol. 64, 19 (1989).

11.   T. K. Choudhury, Y. He, W. A. Sanders, and M. C. Lin, "CO formation in the thermal decomposition of CH_3ONO at high temperatures: Kinetic modeling of the CH_3O decomposition rate", J. Phys. Chem., in press.

12.   C.-Y. Lin and M. C. Lin, "Kinetic modeling of the H + CH_3OH reaction in discharge flow studies: H-atom abstraction rates and H_2O formation mechanism", Combust. Sci. and Tech., submitted.

13.   T. K. Choudhury, M. C. Lin, C.-Y. Lin and W. A. Sanders, "Thermal decomposition of t-C_4H_9OH in shock waves" Combust. Sci. Techn., submitted.

Papers under preparation:

1. Y. He, W. A. Sanders and M. C. Lin "Effect of nitric oxide on the methyl nitrite decomposition reaction: kinetics and mechanisms of the HNO + HNO and HNO + 2NO Reactions", in preparation.

2. Y. He, W. A. Sanders and M. C. Lin, "Effect of NO_2 on the CH_3ONO decomposition reaction", in preparation.

3. C.-Y. Lin, T. K. Choudhury and M. C. Lin, "Kinetic modeling of H_2O and CO formation in the thermal decomposition of CH_3OH", in preparation.

4. Y. He, M. C. Lin and C. F. Melius, "Theoretical interpretation of the mechanism of the HNO + HNO reaction", in preparation.

Measured experimental data under evaluation:

1. Thermal oxidation of CH_3OH in Shock Waves—collaborators: T. K. Choudhury, C.-Y. Lin and M. C. Lin

2. Thermal decomposition and oxidation of C_2H_5OH—collaborators: T. K. Choudhury and M. C. Lin

3. Thermal decomposition of i-C_3H_7OH—collaborators: T. K. Choudhury and M. C. Lin

4. Kinetics and mechanisms of reactions C_6H_5 with O_2 and NO_2—collaborators: C.-Y. Lin and M. C. Lin

5. Kinetics and mechanism of C_6H_6 oxidation in shock waves: time-resolved CO and H_2O production—collaborators: C.-Y. Lin and M. C. Lin

6.   Shock-heating of mixtures of CH_3ONO and CH_3OH—collaborators: T. K. Choudhury, C.-Y. Lin and M. C. Lin

IV.   PRESENTATIONS:

1.   C.-Y. Lin, W. A. Sanders, M. E. Umstead and M. C. Lin, "The kinetics of phenly radical reactions with O_2 and NO_2", 21st Symp. (International) on Combustion, Munuch, W. Germany, Aug. 1986.

2.   Y. He, W. A. Sanders and M. C. Lin, "Kinetics and mechanism of the pyrolysis of methyl nitrite", 20th Fall Technical Meeting, Eastern Section, The Combustion Institute, NBS, Nov. 1987.

3.   T. Choudhury, C.-Y. Lin, W. A. Sanders and M. C. Lin, "Kinetics and mechanism of thermal decomposition of tert-butly alcohol in shock waves", 20th Fall Technical Meeting, Eastern Section, The Combustion Institute, NBS, Nov. 1987.

4.   S. Zabarnick, J. W. Fleming and M. C. Lin, "Kinetics of CH Reactions with N_2O, SO_2, COS and CS_2", 20th Fall Technical Meeting, Eastern Section, The Combustion Institute, NBS, Nov. 1987.

5.   C.-Y. Lin and M. C. Lin, "Kinetics of the $C_6H_5 + O_2$ reaction", 20th Fall Technical Meeting, The Combustion Institute, NBS, Nov. 1987.

6.   M. Page, M. C. Lin, Y. He and T. K. Choudhury, "Kinetics of the CH_3O Decomposition Reaction: Theory and Experiment", The Fall Technical Meeting, The Eastern Combustion Section, Tamp, FL, Dec. 1988.

7.   Y. He, W. A. Sanders, M. C. Lin and C. F. Melius. "Effects of NO on the Thermal Decomposition of Methyl Nitrite: Kinetics and Mechanisms of HNO + HNO and HNO + 2NO". 2nd International Conference on Chemical Kinetics, NIST, July 24-27, 1989.

8.   T. K. Choudhury, W. A. Sanders and M. C. Lin, "The Reaction of CH_2O with H and CH_3 in Shock Waves", 2nd International Chemical Kinetics Conference, NIST, July 24-27, 1989.

V.   Appendices

Reprints and Preprints of papers resulting from the work performed under contract No. DE - FG05 - 85ER13373.

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