The Origin and Fate of Organic Pollutants from the Combustion of Alternative Fuels: Phase III Report

P.H. Taylor, B. Dellinger, M. Rahman

Technical Monitor: Brent Bailey

MASTER

National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, Colorado 80401-3393
A national laboratory of the U.S. Department of Energy
Managed by Midwest Research Institute
for the U.S. Department of Energy
under Contract No. DE-AC36-83CH10093

Prepared under Subcontract No. XAU-3-13013-01

July 1996

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

This publication was reproduced from the best available camera-ready copy submitted by the subcontractor and received no editorial review at NREL.

NOTICE

This report was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or any agency thereof.

Available to DOE and DOE contractors from:
Office of Scientific and Technical Information (OSTI)
P.O. Box 62
Oak Ridge, TN 37831
Prices available by calling (423) 576-8401

Available to the public from:
National Technical Information Service (NTIS)
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161
(703) 487-4650

Printed on paper containing at least 50% wastepaper, including 10% postconsumer waste

DISCLAIMER

**Portions of this document may be illegible
in electronic image products. Images are
produced from the best available original
document.**

The Origin and Fate of Organic Pollutants from the Combustion of Alternative Fuels

Principal Investigators:

Philip H. Taylor, Ph.D.
Barry Dellinger, Ph.D.

Other Contributors

Moshiur Rahman¹

University of Dayton Research Institute
Environmental Sciences and Engineering Group
300 College Park
Dayton, Ohio 45469-0132

Final Report for time period: May 1, 1995 through April 30, 1996
National Renewable Energy Laboratory Subcontract No. XAU-3-12228-02

May 9, 1996

¹M.S. Candidate in Chemical Engineering

Phase III Executive Summary

The overall objective of this project is to determine the impact of alternative fuels on air quality, particularly ozone formation. This objective will be met through three steps: (1) qualitative identification of alternative fuel combustion products; (2) quantitative measurement of specific emission levels of these products; and (3) determination of the fate of the combustion products in the atmosphere, particularly in terms of depletion or conversion by hydroxyl (OH) radical attack. The alternative fuels of interest are methanol, ethanol, natural gas, and liquefied petroleum gas.

The role of the University of Dayton Research Institute (UDRI) in this project is twofold. First, fused silica flow reactor instrumentation is being used to obtain both qualitative identification and quantitative emissions data on the thermal degradation products from the fuel-lean (oxidative), stoichiometric, and fuel-rich (pyrolytic) decomposition of methanol, ethanol, natural gas, and LP gas. Second, a laser photolysis/laser-induced fluorescence apparatus is being used to determine the rates and mechanisms of reaction of selected degradation products under atmospheric and combustion conditions.

In the third year of this study, we have obtained additional rate measurements of the reaction of hydroxyl radical (OH) with alternative fuel combustion by-products over an extended temperature range. New measurements are reported for dimethyl ether, methyl *t*-butyl ether, and acetaldehyde. Room temperature rate coefficients for dimethyl ether were in excellent agreement with previous measurements. Room temperature rate coefficients were ~20% lower and ~20% higher than previous measurements for acetaldehyde and methyl *t*-butyl ether, respectively. For dimethyl ether and methyl *t*-butyl ether, substantial curvature in the Arrhenius plots was observed. The temperature-dependent data for dimethyl ether and methyl *t*-butyl ether are consistent with a H-atom abstraction mechanism. Experimental measurements of the acetaldehyde + OH reaction indicated a complex reaction mechanism. QRRK analyses indicated that OH addition followed by CH₃ elimination was the dominant reaction pathway at temperatures between 295 and 600 K. A small deuterated isotope effect was observed for H-atom abstraction from the carbonyl group at 295 K. This result was consistent with QRRK calculations suggesting that H-atom abstraction from the ketyl group is a minor pathway at these temperatures. The experimental and modeling results indicate that the dominant reaction channel at combustion temperatures is H-atom abstraction from the methyl group.

Table of Contents

	<u>Page</u>
Phase III Executive Summary	ii
List of Figures	iv
List of Tables	v
Introduction	1
Task 2-Elementary Reaction Kinetic Studies of OH with Exhaust Products over an Extended Temperature Range	2
Experimental Approach and Data Reduction	2
Experimental Results	4
Discussion	6
References	16

List of Figures

	<u>Page</u>
1. Schematic of LP/LIF system (left) and optical test cell (right).	3
2. Arrhenius plot of experimental rate measurements for $\text{CH}_3\text{OCH}_3 + \text{OH}$	7
3. Arrhenius plot of experimental rate measurements for $\text{CH}_3\text{OC}(\text{CH}_3)_3 + \text{OH}$	8
4. Arrhenius plot of experimental rate measurements for $\text{CH}_3\text{CHO} + \text{OH}$	10
5. Arrhenius plot of QRRK model results for k_1 . k_{1a} : OH addition/ CH_3 elimination, k_{1b} : OH addition/H elimination, k_2 : H-atom abstraction from ketyl group, k_3 : H-atom abstraction from $-\text{CH}_3$ group, k_{tot} : sum of calculated rate coefficients for all channels, k_{exp} : experimental observed rate coefficients. The calculated rate coefficients for stabilization of the $\text{OH} + \text{CH}_3\text{CHO}$ adduct were less than $1 \times 10^{10} \text{ cm}^3/\text{mol-s}$ and are not shown.	12

List of Tables

	<u>Page</u>
1. Absolute Rate Coefficients for $\text{CH}_3\text{OCH}_3 + \text{OH}$ (in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). . . .	4
2. Absolute Rate Coefficients for $\text{CH}_3\text{OC}(\text{CH}_3)_3 + \text{OH}$ (in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). . .	5
3. Absolute Rate Coefficients for $\text{CH}_3\text{CHO} + \text{OH}$ (in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). . . .	6
4. Deuterated Isotope Data	13
5. OH Reactivity of Oxygenated, Alternative Fuel By-products.	14
6. Atmospheric Lifetimes of Oxygenated, Alternative Fuel By-products.	15

Introduction

The National Renewable Energy Laboratory (NREL) is the field manager for the U.S. Department of Energy (DOE) Alternative Fuels Utilization Program (AFUP). The goal of the AFUP is to develop and advance technology that allows an effective, optimum use of nonpetroleum-based transportation fuels, while complying with modern constraints, such as vehicle emissions. For alternative fuels to be viable candidates to replace petroleum-based counterparts, it must be demonstrated that their impact on air quality will be no worse than that of existing fuels and preferably show characteristics that will improve air quality. To make this determination, an extensive program is necessary to identify the atmospheric reactivity of the exhaust species from alternative fuels. For comparison purposes, similar analyses are being performed on advanced petroleum-based fuels.

Because of the nation's continuing concern about air pollution, Congress enacted the Clean Air Act Amendments of 1990. The provisions will force broad changes in fuels and vehicles. For example, reformulated gasolines and alternative fuels are receiving wide attention as industry struggles to comply with the amendments. At the same time, there are many basic scientific questions about the benefits of switching to alternative fuels. The scientific community does not adequately understand the durability and emission performance of candidate alternative fuels. Additional research is needed, including the ultimate impact on air quality, to identify acceptable alternatives for conventional transportation fuels.

The overall objective of this project is to determine the impact of alternative fuels on air quality, particularly ozone formation. The objective will be met through three steps: (1) qualitative identification of alternative fuel combustion products, (2) quantitative measurement of specific emission levels of these products, and (3) determination of the fate of the combustion products in the atmosphere. The alternative fuels of interest are methanol, ethanol, natural gas, and liquefied petroleum (LP) gas.

The role of the University of Dayton Research Institute (UDRI) in this project is twofold. First, fused silica flow reactor instrumentation is being used to obtain both qualitative identification and quantitative data on the thermal degradation products from the fuel-lean (oxidative), stoichiometric, and fuel-rich (pyrolytic) decomposition of methanol, ethanol, liquefied petroleum gas, and natural gas. Second, a laser photolysis/laser-induced fluorescence (LP/LIF) apparatus is being used to determine the rates and mechanisms of reaction of selected degradation products under atmospheric conditions.

This draft final report contains the results of the third year of the study.

Task 2-Elementary Reaction Kinetic Studies of OH with Exhaust Products over an Extended Temperature Range

The objective of these experiments is to measure elementary reaction rate coefficients for the reaction of OH radicals with representative combustion by-products of alternative fuels at temperatures relevant to tropospheric chemistry and the combustion of these compounds, i.e., 295-1000 K. Rate coefficients are being measured with a single apparatus using a modified laser photolysis/laser-induced fluorescence (LP/LIF) technique.

The experiments discussed in the ensuing paragraphs are attempting to address the following issues:

- (1) Identification of systematic error in previous low temperature measurements and improvement of the alternative fuel-OH reaction kinetic data base pertaining to tropospheric lifetimes.
- (2) Identification of multiple mechanisms of reaction and any change in mechanism with temperature;
- (3) Improvement of application of transition state theory formalism to modeling of bimolecular reactions over extended temperature ranges;
- (4) Elucidation of structure-activity relationships for reactions of alternative fuels and exhaust by-products with OH;
- (5) Development of improved detailed, elementary reaction kinetic models of alternative fuel combustion; and

To address these issues, we are using a refined LP/LIF technique for the measurement of OH-alternative fuel reaction kinetics over an extended temperature range. The major advantages of this technique, as described in the following paragraphs, are:

- (1) Capability to measure reaction rate constants over an extended temperature range using a single apparatus;
- (2) Generation of a clean source of OH radicals;
- (3) Capability of atmospheric pressure measurements;
- (4) Extensive purification and analysis of all reactants;
- (5) Capability to thoroughly analyze potential photolysis-based secondary reactions.

Experimental Approach and Data Reduction

The experimental procedures were very similar to previous studies of OH reactions with chlorinated hydrocarbons (Jiang et al., 1992, 1993a, 1993b) and hydrochlorofluorocarbons (Fang et al., 1996). As a result, we only briefly summarize the procedures here.

OH radicals were produced by 193.3 nm photodissociation of $\text{N}_2\text{O}/\text{H}_2\text{O}/\text{He}$ gas mixtures with a ArF excimer laser (Questek Model 2860). Initial OH concentrations, $[\text{OH}]_0$, ranged from 4×10^{10} to 4×10^{11} molecules cm^{-3} and were determined from published values of the N_2O absorption coefficient (8.95×10^{-20} cm^2 molecule $^{-1}$ at 298 K), (Selwyb et al., 1977) a photodissociation quantum yield for $\text{O}(^1\text{D})$ production of unity, (Simonaitis and Heicklen, 1973) and the rapid reaction of $\text{O}(^1\text{D})$ with H_2O (95% conversion in < 20 μs). Experiments were conducted for photolysis laser intensities of 1-10 mJ cm^{-2} . Following reaction initiation, time-resolved OH profiles were measured as functions of reactant concentration using laser-induced fluorescence with a pulsed Nd:YAG pumped dye laser (Quanta Ray Model DCR-2/PDL-2) emitting at the wavelength of 282.1 nm. Broadband fluorescence was collected at 309 nm using a PMT/bandpass filter combination.

Figure 1. Schematic of LP/LIF system (left) and optical test cell (right).

In order to control the temperature uniformly, four symmetrical ceramic heaters surround the optical reactor adjacent to the reaction zone. The gas temperature was measured with a chromel-alumel thermocouple positioned ~ 3 mm from the probe intersection volume. Measurements using a second retractable chromel-alumel thermocouple indicated a variation of less than 3 K across the detection volume for gas temperatures ranging from 295 K to 1000 K. All experiments were carried out under slow flow conditions and the buildup of reaction products was minimized. Individually controlled gas flows of [Reactant]/N₂O/H₂O/He were thoroughly mixed before entering the optical reactor. The composite flow conditioned the reactor for 1-3 minutes prior to the onset of data collection, thereby minimizing any effects due to reactant adsorption on the reactor walls. A majority of the experiments were conducted at a total pressure of 740 ± 10 torr. For acetaldehyde (CH₃CHO), additional experiments were conducted at pressures of 100, 300, and 400 torr. Pressures were measured with a calibrated vacuum gauge. Flow rates were controlled with differential flow transducers and were checked following each experiment using the soap bubble technique. To provide additional information on the mechanism of reaction of OH + CH₃CHO, measurements for CH₃CDO and CD₃CDO were also obtained over an extended range of temperatures at a pressure of 740 torr helium.

For all experiments, reactive and diffusive OH radical decay profiles exhibited exponential behavior and were fitted by the following nonlinear expression

$$[\text{OH}] = [\text{OH}]_0 \exp(-k't) + \gamma,$$

where γ is the constant background signal level and t is the time delay between the two lasers. Because $[\text{reactant}] > 1000[\text{OH}]$ in all reactive experiments, exponential OH radical decays, of pseudo-first-order decay constant $k' = k[\text{reactant}] + k_d$, were observed. k_d is the first order rate constant for OH radical disappearance from the probe volume due to diffusion and reaction with impurities in the carrier gas. The bimolecular rate constant, k , was obtained from the slope of the least-squares straight line through the graph of k' versus $[\text{reactant}]$.

During the second year of this study, we have focused on the following alternative fuel by-products: CH_3CHO (and the deuterated samples CH_3CDO and CD_3CDO), dimethyl ether (CH_3OCH_3), and methyl *t*-butyl ether ($\text{CH}_3\text{OC}(\text{CH}_3)_3$). Stock samples were obtained from Aldrich, Inc. Gas chromatography-mass spectrometry (GC/MS) analyses indicated the stock samples were largely free of contaminants (>99.9% pure). The remaining chemicals used in our gas delivery system had the following stated minimum purities: He (99.999+%); N_2O (99.9%); H_2O (HPLC organic-free reagent grade). Absorption cross sections for the reactants were very small (on the order of $10^{-21} \text{ cm}^2 \text{ molecule}^{-1}$ or less) (Lake and Harrison, 1959, Calvert and Pitts, 1967) in comparison with N_2O at 193 nm. Thus, laser photolysis of the reactants was expected to be insignificant. This was verified by numerous experiments where variation of the excimer laser intensity had no observable effect on OH decays.

Experimental Results

Dimethyl ether + OH

Measurements for the reaction of OH radicals with CH_3OCH_3 between temperatures of 295 and 753 K are summarized in Table 1.

Table 1
Absolute Rate Coefficients for CH_3OCH_3 (in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)

Temp, K	$10^{12} k$	$10^{12} \sigma_k$
295	2.946	0.21
346	3.701	0.26
346.5	3.419	0.18
396	3.726	0.20
455	4.198	0.11
490	4.618	0.25
549	6.275	0.31
601	7.119	0.47
650	8.194	0.39
700	7.295	0.25
753	7.923	0.43

Measurements at temperatures of 700 K and 750 K resulted in lower rate constants ($\sim 7 \times 10^{-12} \text{ cm}^3/\text{molec-s}$). This deviation was attributed to thermal decomposition of the reactant. Ninety-five percent confidence intervals, as determined by a propagation of error analysis, ranged from $\pm 5\%$ to $\pm 14\%$. To our knowledge, this is the first report of experimental measurements for this reaction above temperatures of 450 K.

Methyl t-butyl ether + OH

Initial measurements of the reaction of OH with methyl *t*-butyl ether ($\text{CH}_3\text{OC}(\text{CH}_3)_3$) produced accurate rate coefficients between 298-450 K (see Table 2).

Table 2
Absolute Rate Coefficients for $\text{CH}_3\text{OC}(\text{CH}_3)_3$ (in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)

Temp, K	$10^{12} k$	$10^{12} \sigma_k$
Exp. # 1		
300	2.83	0.30
350	3.23	0.55
400	3.26	0.35
450	3.99	0.67
Exp. # 2		
298	3.66	0.21
350	4.06	0.40
400	4.50	0.22
450	4.95	0.29
500	5.72	0.28
550	6.10	0.32
600	6.93	0.38
650	7.98	0.37
700	8.69	0.36
750	9.42	0.36
800	10.44	0.89

Measurements above 450 K did not produce a linear relationship between pseudo-first-order rate constant, k' , and reactant concentration and were interpreted to indicate thermal decomposition of the sample. Ninety-five percent confidence intervals, as determined by a propagation of error analysis, ranged from $\pm 21\%$ to $\pm 34\%$.

Additional measurements of the $\text{OH} + \text{CH}_3\text{OC}(\text{CH}_3)_3$ reaction were conducted with the goal of obtaining data at higher temperatures ($>450 \text{ K}$). The latest set of experiments were performed at higher total gas flow rates to minimize thermal decomposition of the sample. The results are also summarized in Table 2. Measurements were obtained from 295-800 K. Ninety-five percent confidence intervals, as determined by a propagation of error analysis, ranged from $\pm 10\%$ to $\pm 18\%$. To our knowledge, this is the first report of experimental measurements for this reaction above temperatures of 450 K. At 850 K, non-exponential OH decays were observed. This was attributed to thermal decomposition of the sample.

The latter experiments produced rate coefficients about 20% larger than initially observed. GC-MS analysis of the stock sample indicated very small ($<0.1\%$) amounts of methyl formate and methyl alcohol as impurities. These impurities react with OH at a much slower rate and as such did not affect the rate measurements. We have also checked the stability of the sample in our light-tight Pyrex sample bulbs. A 10% decrease in room temperature rate measurements was observed using a sample stored for 24 hr in the Pyrex sample bulb. All of the data shown in exp. #2 were obtained with fresh reactant samples (sample storage of $<6 \text{ hrs}$). However, some of the data obtained in exp. #1 (including the multiple room temperature measurements) were obtained with samples stored in glass vessels for more than 24 hrs. Surface absorption may thus partially account for the lower measured rate coefficients under these conditions.

Acetaldehyde + OH

Absolute rate measurements for the reaction of OH with CH_3CHO were obtained from 295-900 K. 2σ error limits, based on a propagation of error analysis, ranged from $\pm 8\%$ to $\pm 27\%$. The experimental results are presented in Table 3.

Table 3
Absolute Rate Coefficients for CH₃CHO (in cm³ molecule⁻¹ s⁻¹)

Temp, K	10 ¹² k	10 ¹² σ _k
298	12.3	1.10
350	10.3	0.55
400	9.37	0.80
450	8.58	0.93
500	8.00	0.96
550	7.60	0.74
600	7.06	0.30
650	7.26	0.84
700	7.58	0.74
750	7.95	0.85
800	8.38	0.67
850	8.79	1.20
900	9.17	1.03

The rate coefficients determined from these measurements were 22% smaller than Atkinson's recommendation (Atkinson, 1989) based on previous measurements yet in good agreement with the measurements of Semmes et al. (1985). Low rate coefficient measurements may be ascribed to absorption of CH₃CHO on the surface of the sample storage bulbs. GC analysis of our sample bulbs did not show a decrease in reactant concentration over an eight hour time period during which the samples were used. A slight decrease (~20%) in reactant concentration was observed over a three-day period. A related finding was reported by Semmes et al. (1985). The lower rate coefficients observed in both of these studies are not believed to be caused by surface absorption.

Discussion

Reaction with OH radicals is an important step in the oxidation of organic compounds in the atmosphere (Finlayson-Pitts and Pitts, 1986) and in combustion systems (Warnatz, 1984). Oxygenated hydrocarbons are being added to fuels to maintain performance by increasing octane while simultaneously lowering tailpipe emissions of CO (US-EPA, 1988). However, to understand the impact of such additives on the atmospheric reactivity of tailpipe and evaporative emissions, the mechanism of their atmospheric oxidation must be understood. In addition, since these oxygenated hydrocarbons are being used as fuel additives, their reactions and mechanism of oxidation under combustion conditions is also of interest. In this section, we discuss the reactivity and reaction mechanisms of alternative fuel by-products under both atmospheric and post-combustion conditions.

CH₃OCH₃ + OH

There have been six prior studies of the gas-phase reaction of OH radicals with CH₃OCH₃ (Perry et al., 1977, Tully and Droege, 1987, Wallington, et al. 1988a, Melliuki et al., 1995, Nelson, et al., 1990, Wallington, 1989). Four of these studies have been conducted as a function of temperature, with the experiments of Tully and Droege (1987) considered the most accurate. The results are summarized in Figure 2.

Figure 2. Arrhenius plot of experimental rate measurements for $\text{CH}_3\text{OCH}_3 + \text{OH}$.

The available temperature-dependent data were best described by a simple Arrhenius expression. This reaction proceeds by H-atom abstraction from the $-\text{CH}_3$ groups. The rate coefficient per C-H bond for CH_3OCH_3 is similar to that of the reaction of OH radicals with secondary C-H bonds in alkanes (Perry et al. 1977). This is to be expected, because the C-H bond strength in CH_3OCH_3 is $93 \pm 1 \text{ kcal/mol}$, similar to the secondary C-H bond strength in n-butane of $95 \pm 1 \text{ kcal/mol}$. Tully and Droege (1987) attempted to acquire data above 440 K, but unidentified secondary processes interfered with the kinetics. Room temperature product analysis studies under atmospheric conditions indicated that methyl formate was the only observable product (accounting for >90% of dimethyl ether conversion) (Japar et al., 1990).

We have obtained measurements for the reaction of OH radicals with CH_3OCH_3 between temperatures of 295 and 650 K. A comparison of these measurements with previous measurements is shown in Figure 2. The rate constant measurements between 295 K and 450 K are in excellent agreement with the previous measurements of Tully and Droege (1987) and the recommended Arrhenius expression given by Atkinson (1989). The rate constant measurements of Perry et al. (1977) and Wallington et al. (1988) are displaced approximately equally above and below the most

recent LP/LIF measurements. Above 500 K, significant curvature in the Arrhenius plot was observed. The recommended, empirical best fit, based on our measurements and those of Tully and Droege (1987) (see Figure 2) is given by the following modified Arrhenius expression:

$$k \text{ (295-650 K)} = 7.73 \times 10^{-21} T^{3.04} \exp(738.0/T) \text{ cm}^3/\text{molec}\cdot\text{s}.$$

The temperature exponent ($n = 3.04$) is within the realm of transition state theory predictions for a nonlinear transition state (Cohen, 1989).

$\text{CH}_3\text{OC}(\text{CH}_3)_3 + \text{OH}$

There have been four prior measurements of the gas-phase reaction of OH radicals with methyl *t*-butyl ether ($\text{CH}_3\text{OC}(\text{CH}_3)_3$) (Cox and Goldstone, 1982, Wallington et al. 1988b, Bennett and Kerr, 1990, Smith et al., 1991). The results are summarized in Figure 3.

Figure 3. Arrhenius plot of experimental rate measurements for $\text{CH}_3\text{OC}(\text{CH}_3)_3 + \text{OH}$.

The room temperature data from these four studies are in reasonably good agreement. The reports of Wallington et al. (1988b) and Bennett and Kerr (1990) represent the only temperature-dependent studies. The activation energy derived from the Bennett and Kerr (1990) study was about one-half of the Wallington et al. (1988b) study. The reaction proceeds by H-atom abstraction. Product analysis in smog chamber experiments at room temperature indicated that H-atom abstraction from the -OCH₃ group and the *t*-butyl group accounted for ~70-85% and ~20% of the overall reaction, respectively (Japar et al., 1990, Tuazon et al., 1991).

Our initial set of experimental results were in very good agreement with previous measurements. The rate measurement at 300 K (2.83×10^{-12} cm³/molec-s) was identical to the room temperature recommendation of Atkinson (1989). Our latter experiments resulted in rate coefficients about 20% larger than previously reported. A non-linear least-squares analysis of the latter temperature-dependent data indicated non-Arrhenius behavior as indicated by the following best fit expression (see Figure 3):

$$k(295-800 \text{ K}) = 1.44 \times 10^{-17} T^{1.94} \exp(396/T) \text{ cm}^3/\text{molec-s}.$$

The value of the temperature exponent ($n = 1.94$) is within the realm of transition state theory predictions for a nonlinear transition state (Cohen, 1989).

Acetaldehyde + OH

There have been a number of studies of the reaction of OH radicals with CH₃CHO (Atkinson and Lloyd, 1984, Michael et al., 1985, Morris et al., 1971, Morris and Niki, 1971, Niki et al., 1978, Kerr and Sheppard, 1981, Atkinson and Pitts, 1978, Semmes et al., 1985, Dobe et al., 1989, Balestra-Garcia et al., 1992, Scollard et al., 1993, Tyndall et al., 1995). However, all of these measurements have been limited to relatively low temperatures (<540 K) and have been conducted to understand the mechanism of oxidation of CH₃CHO under atmospheric conditions.

The mechanism of reaction under atmospheric and higher temperature conditions characteristic of combustion remains poorly understood due to the lack of definitive product and mechanistic data. Atkinson and Lloyd (1984) reported the formation of PAN from the room temperature reaction of OH with CH₃CHO in air in the presence of NO_x. They reported that the following mechanism involving H-atom abstraction was consistent with their observations:

Because this mechanism involves abstraction of the sole ketyl (CHO) hydrogen, it is consistent with the observation that the room temperature rate coefficients for the $\geq \text{C}_2$ aldehydes are reasonably similar, increasing only slightly with the length of the alkyl side chain and showing that the alkyl substituent has only a minimal effect on the OH radical rate coefficient. They also proposed that the negative temperature dependence of the OH rate constant reported by several researchers (Michael et al., 1985, Atkinson and Pitts, 1978, Semmes et al., 1985) (cf. Figure 4) indicates that although the reaction proceeds by overall H-atom abstraction, the reaction involves initial OH radical addition followed by rapid decomposition of the adduct to the observed products.

Prior to this study, there were no measurements reported above 538 K. Our experimental measurements span a temperature range of 295-900 K. Above 600 K, our measurements indicate a change in temperature dependence from negative to positive. Above 900 K, experimental measurements were not possible due to thermal decomposition of the sample. The experimental results for the two apparently different mechanisms of reaction were well represented by the following simple Arrhenius expressions:

$$\begin{aligned} k_{295-550 \text{ K}} &= (4.31 \pm 0.22) \times 10^{-12} \exp[(309 \pm 19)/T] \text{ cm}^3/\text{molec-s}. \\ k_{600-900 \text{ K}} &= (1.89 \pm 0.26) \times 10^{-11} \exp[(-597 \pm 108)/T] \text{ cm}^3/\text{molec-s}. \end{aligned}$$

where error limits represent $\pm 2\sigma$ (95% confidence intervals).

The negative temperature dependence of this reaction is well established by this study and earlier work (Michael et al., 1985, Atkinson and Pitts, 1978, Semmes et al., 1985, Dobe et al. 1989). This observation immediately suggests the possibility of an addition-elimination mechanism for reaction (1) at low temperatures (<600 K), e.g.

since many addition reactions of OH show overall negative temperature dependence at these temperatures (Atkinson, 1989). Reaction (1) would undoubtedly proceed through a vibrationally excited adduct that would be expected to undergo collisional stabilization $\beta k_s[\text{M}]$ in addition to forward (k_{1a} or k_{1b}) and reverse (k_{-1}) decompositions. A pathway analogous to rxn (1b) has already been suggested in the related formaldehyde (HCHO) case (Horowitz and Calvert, 1978).

Figure 4. Arrhenius plot of experimental rate measurements for OH + CH₃CHO.

To examine the possibility of OH addition, we have obtained rate measurements at 100, 300, and 400 torr, in addition to our atmospheric pressure measurements, at temperatures of 295 and 600 K. The results, presented in Figure 4, indicate no pressure dependence for reaction (1). The good agreement between the low pressure DF-RF results (Atkinson and Pitts, 1978) and the higher pressure FP-RF results (Michael et al., 1985) are consistent with our experimental observations. Hence, if the adduct path exists, either the adduct is always stabilized and reaction (1) is in the high pressure limit above 1.5 torr helium, or the forward dissociation paths to either acetic acid and H atoms or formic acid and methyl radicals are much faster than the average dissociation path back to reactants. Michael et al. (1985) ruled out reaction (1b) on the basis of H atom scavenger experiments using NO₂. However, they could not rule out reaction (1a) using the same approach because of competing secondary reactions. They noted that the overall exothermicity to CH₃ + HCOOH was 3.8 kcal/mol lower than that to H + CH₃COOH (-26.2 and -22.4 kcal/mol, respectively (Wagman et al. 1982).

A completely different alternative to the displacement reactions just considered is the direct metathetical abstraction process that would appear consistent with the positive temperature dependent rate data observed above 600 K:

Reaction (2) is considered to be more likely because the carbonyl H-atom bond strength is much lower than that for methyl (86.4 compared to ~98 kcal/mol, respectively). Indeed, acetyl (CH₃CO) radicals were the only observed radicals in the related Cl-atom abstraction reaction (Slagle and Gutman, 1982).

The two alternatives thus suggest that either stabilized adduct radicals, HCOOH + CH₃ formation, or acetyl radicals are the most probable products of reaction (1). To examine carefully the possibilities of chemically-activated OH addition versus H-atom abstraction, Quantum RRK calculations (Westmoreland et al., 1986, Dean and Westmoreland, 1986) were carried out for reaction (1) using *ab initio* modeling (Hehre et al, 1986, Frisch et al, 1992, Curtiss et al, 1991, 1993, Foresman and Frisch, 1993) and thermochemical transition state theory (TST) calculations (Benson, 1976, Laidler, 1987) of the critical high pressure limit rate parameters. The reader is referred to Taylor et al. (1996) for details of these calculations. The results of the QRRK calculations at 740 torr helium pressure are shown in Figure 5.

Figure 5. Arrhenius plot of QRRK model results for OH + CH₃CHO. k_{1a} : OH addition/CH₃ elimination, k_{1b} : OH addition/H elimination, k_2 : H-atom abstraction from carbonyl group, k_3 : H-atom abstraction from -CH₃ group, k_{tot} : sum of calculated rate coefficients for all channels, k_{exp} : experimentally observed rate coefficients. The calculated rate coefficients for stabilization of the OH + CH₃CHO adduct were less than 1×10^{10} cm³/mol-s and are not shown.

Rate coefficients for H-atom elimination, CH₃ elimination, H-atom abstraction from the carbonyl group, and H-atom abstraction from the -CH₃ group are shown along with the sum of these channels and the experimental measurements. The agreement between the measured and calculated total rate coefficient is very good. The rate coefficient for stabilization of the adduct is much smaller in magnitude than the other reaction channels and is not shown.

The QRRK calculation demonstrated a complex coupling of four reaction channels as a function of temperature. Methyl radical elimination dominated the observed rate measurements below temperatures of 650 K. H-atom abstraction from the ketyl group accounted for approximately 10% of the observed rate at 295 K. Above 650 K, the dominant reaction channel was H-atom abstraction from the CH₃ group. At 900 K, the relative contributions of H-atom abstraction from the CH₃

group, CH₃ elimination, and H-atom abstraction from the ketyl group were 55%, 28%, and 17% of the observed rate. QRRK calculations indicated that the significant reaction channels (all except adduct stabilization) were independent of total pressure. This result is consistent with experimental measurements.

To determine whether the mechanistic implications of the QRRK calculations described were plausible, additional rate coefficient measurements were performed using deuterated and perdeuterated reactants. The measured rate coefficients for CH₃CDO and CD₃CDO, obtained at 740 torr total helium pressure, at temperatures of 295, 400, 600, and 750 K, are presented in Table 4. Error limits, 2σ, based on a propagation of error analysis, ranged from ±4% to ±20%. Also given in Table 4 are the respective kinetic isotope ratios, kCH₃CHO/kCH₃CDO and kCH₃CHO/kCD₃CDO. Measurable kinetic isotope effects were observed for CH₃CDO at room temperature and for CD₃CDO at all four temperatures. Of particular significance was the observed kinetic isotope effect for CH₃CDO at room temperature, indicating that H-atom abstraction from the ketyl group does occur. This result also supports the findings of the *ab initio* calculations suggesting the lack of an appreciable barrier to this reaction. At elevated temperatures, the observed kinetic isotope effect for CD₃CDO is consistent with model predictions regarding the increased importance of H-abstraction from CH₃ at elevated temperatures.

Table 4
Deuterated Isotope Data^a

T, K	kCH ₃ CHO	kCH ₃ CDO	kCD ₃ CDO	kCH ₃ CHO/kCH ₃ CDO	kCH ₃ CHO/kCD ₃ CDO
298	1.23 x 10 ⁻¹¹	9.42 x 10 ⁻¹²	1.02 x 10 ⁻¹¹	1.31	1.21
400	9.38 x 10 ⁻¹²	8.95 x 10 ⁻¹²	7.85 x 10 ⁻¹²	1.05	1.19
600	7.41 x 10 ⁻¹²	7.35 x 10 ⁻¹²	6.02 x 10 ⁻¹²	1.01	1.23
750	8.52 x 10 ⁻¹²	8.65 x 10 ⁻¹²	7.28 x 10 ⁻¹²	0.98	1.17

^a Units of cm³ molecule⁻¹ s⁻¹.

The reported measurements and QRRK analysis of the CH₃CHO + OH reaction indicate that OH addition followed by CH₃ elimination is the dominant reaction pathway at temperatures between 295 and 600 K. The deuterated isotope studies support the previous contention of Atkinson and Lloyd (1984) that H-atom abstraction from the carbonyl group does occur at temperatures pertinent to atmospheric conditions. However, both the small deuterium isotope effect and the QRRK calculations suggest that this is a minor pathway. Our calculations also support the findings of Michael, et al. (1985), that is, the H-atom elimination pathway is largely insignificant, except possibly at the lowest temperatures. The dominant reaction channel at combustion temperatures is postulated to be H-atom abstraction from the methyl group. The branching ratios for the various reaction channels derived from the QRRK calculations must be considered with caution, due primarily to the uncertainty in the estimated rate parameters for k₂. Variational transition state theory analysis (Garrett et al, 1981) of k₂ is necessary to quantify this unusual H-atom abstraction reaction more carefully.

At first glance, the new results presented in this report appear at odds with prior smog chamber experiments where observation of PAN and HCHO formation from irradiation of NO_x-CH₃CHO-air mixtures suggested that the initial reaction involved CH₃CO radical formation. Although our new results do not completely rule out the low temperature H-atom abstraction pathway, the small deuterium isotope effect is consistent with QRRK calculations which suggest that H-atom abstraction from the ketyl group is a minor pathway and CH₃ elimination is the major pathway. It should be noted that atmospheric oxidation of CH₃ radicals can readily lead to formation of one of the observed products, HCHO, as shown below:

The precursors to PAN, CH_3CO radicals, can subsequently be formed from reaction of CH_3 radicals with CO, an atmospheric oxidation product of HCHO. It is thus conceivable that CH_3 radical production can also result in the production of the previously identified products of CH_3CHO oxidation in smog chamber studies.

Alternative Fuel By-Product Reactivity

Table 5 summarizes our OH rate measurements of alternative fuels and their by-products. Rate measurements at 295 K (room temperature) and 1000 K (representative of post-cylinder combustion conditions) are presented along with recommended measurements at room temperatures based on prior studies (Atkinson, 1989) and the relative deviation between our measurements and the recommended literature measurements (Δk). With the exception of our acetaldehyde and MTBE data (where our measured rate is ~22% lower and ~22% higher than the literature recommendation, respectively), our measurements are in excellent agreement with room temperature recommendations. It is interesting to note the similarity in room temperature reactivities of ethanol and the two ether compounds tested. The rates vary by less than 10%. The rate measurements for acetaldehyde (and presumably formaldehyde) are about a factor of 3-4 higher at room temperature. At 1000 K, there is no prior data available for comparison excluding formaldehyde. Our measured rates for both the alcohol fuels and the ether compounds increase, yet the increase is substantially greater for the ether compounds. For both types of compounds, the most favorable site for H abstraction is adjacent to the oxygen functionality. Since the C-H bond energies are lower for the ether compounds, the larger temperature dependence must be due to a highly nonlinear transition state (strongly temperature dependent pre-exponential factor) for these compounds. The rates for acetaldehyde and formaldehyde are about equal at 1000 K and 295 K. This is due to a change in mechanism from OH addition at lower temperatures (with a near-zero or slightly negative temperature dependence) to H abstraction above 600 K (with a positive temperature dependence).

Table 5
OH Reactivity of Oxygenated, Alternative Fuel By-products

Compound	T, K	$k \times 10^{12}, \text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$	$k_{\text{lit.rec.}} \times 10^{12}, \text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$	Δk
Methanol	295	1.02	0.932	+0.094
Ethanol	295	3.10	3.27	-0.052
Methanol	1000	8.28		
Ethanol	1000	8.37		
Formaldehyde	295		9.78	
Acetaldehyde	295	12.35	15.93	-0.225
Formaldehyde	1000		23.90	
Acetaldehyde	1000	10.21		
Dimethyl ether	295	3.01	2.98	-0.010
MTBE	295	3.46	2.83	+0.223
Dimethyl ether	1000	23.05		
MTBE	1000	14.17		

Oxygenated, Alternative Fuel By-Products: Atmospheric Lifetimes

Table 6 presents atmospheric lifetimes (τ) for methanol, ethanol, acetaldehyde, dimethyl ether, and methyl *t*-butyl ether based on our experimental measurements. Formaldehyde is also shown based on

Atkinson's recommended room temperature rate coefficient. An average atmospheric OH concentration of 2×10^6 molecules cm^{-3} was used for these calculations. As expected, methanol has the longest lifetime (~5.7 days) with the acetaldehyde having the shortest (~0.5 day).

Table 6
Atmospheric Lifetimes (based on OH attack) For
Oxygenated, Alternative Fuel By-products

Compound	τ (days)
Methanol	5.67
Ethanol	1.87
Dimethyl ether	1.92
Methyl <i>t</i> -butyl ether	1.67
Acetaldehyde	0.47
Formaldehyde	0.59

The reaction rates of OH radicals with methanol and ethanol, their primary reaction by-products, that is formaldehyde and acetaldehyde, and oxygenated ether additives to petroleum-derived gasoline are very fast. The reaction rates of OH radicals with the secondary reaction by-products of these compounds, that is, methyl formate, *t*-butyl formate, ethyl formate, *t*-butyl formate, methyl acetate, etc., under atmospheric and combustion conditions are less well characterized and warrant additional study.

References

- Atkinson, R., (1989). J. Phys. Chem. Ref. Data, Monograph 1.
- Atkinson, R. and Lloyd, A.C. (1984). J. Phys. Chem. Ref. Data 13, 315.
- Atkinson, R. and Pitts Jr., J.N. (1978). J. Chem. Phys. 68, 3581.
- Balestra-Garcia, C., LeBras, G., and MacLeod, H. (1992). J. Phys. Chem. 96, 3312.
- Bennett, P.J. and Kerr, J. A. (1990). J. Atmos. Chem. 10, 29.
- Benson, S.W. 1976. *Thermochemical Kinetics*, 2nd ed., Wiley: New York.
- Calvert, J.G. and Pitts, J.N., Jr. (1967). *Photochemistry*, 2nd ed., Wiley: New York.
- Cohen, N. (1989). Int. J. Chem. Kinet., 21, 909.
- Cox, R.A. and Goldstone, A. (1982). Proceedings, Second European Symposium on the Physico-Chemical Behavior of Atmospheric Pollutants, D. Riedel Publishing Co., Dordrecht, Holland, p. 112.
- Curtiss, L. A., Raghavachari, K., Trucks, G. W., Pople, J. A. (1991). J. Chem. Phys. 94, 7221.
- Curtiss, L. A., Raghavachari, K., Pople, J. A. (1993). J. Chem. Phys. 98, 1293.
- Dean, A.M. and Westmoreland, P.R. (1987). Int. J. Chem. Kinet. 19, 207.
- Dobe, S., Khachatryan, L.A., and Berces, T. (1989). Ber. Bunsenges. Phys. Chem. 93, 847.
- Fang, T.D., Taylor, P.H., and Dellinger, B. (1996). in press, J. Phys. Chem.
- Finlayson-Pitts, B.J. and Pitts, Jr., J.N. (1986). *Atmospheric Chemistry*, Wiley: New York.
- Foresman, J. B., Frisch, A.E. (1993). *Exploring Chemistry with Electronic Structure Methods*, Gaussian: Pittsburgh.
- Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. (1992). *Gaussian 92*, Gaussian: Pittsburgh.
- Garrett, B. C., Truhlar, D. G., Grev, R. S. (1981). *Potential Energy Surfaces and Dynamical Calculations* (Ed., Truhlar, D. G.) Plenum: New York.
- Hehre, W. J., Radom, L., Schleyer, P. v. R., Pople, J. A. (1986). *Ab Initio Molecular Orbital Theory*, Wiley: New York.
- Horowitz, A., Su, F., and Calvert, J.G. (1978). Int. J. Chem. Kinet. 10, 1099.
- Japar, S.M., Wallington, T.J., Richert, J.F.O., and Ball, J.C. (1990). Int. J. Chem. Kinet. 22, 1257.
- Jiang, Z., Dellinger, B., and Taylor, P.H. (1992). J. Phys. Chem. 96, 8961.
- Jiang, Z., Dellinger, B., and Taylor, P.H. (1993a). Int. J. Chem. Kinet. 25, 9.
- Jiang, Z., Taylor, P.H., and Dellinger, B. (1993b). J. Phys. Chem. 97, 5050.
- Kerr, J.A. and Sheppard, D.W., (1981). Environ. Sci. Technol. 15, 960.

- Laidler, K.J. (1987). *Chemical Kinetics*, 3rd ed., Harper: New York.
- Lake, J.S. and Harrison, A.J. (1959). *J. Chem. Phys.* 30, 361.
- Melliuki, A., Teton, S., and Le Bras, G. (1995). *Int. J. Chem. Kinet.* 27, 791.
- Michael, J.V., Keil, D.G., and Klemm, R.B. (1985). *J. Chem. Phys.* 83, 1630.
- Morris, Jr., E.D. and Niki, H. (1971). *J. Phys. Chem.* 75, 3640.
- Morris, Jr., E.D., Stedman, D.H., and Niki, H. (1971). *J. Amer. Chem. Soc.* 93, 3570
- Nelson, L., Rattigan, O., Neavyn, R., Sidebottom, H., Treacy, J. and Nielsen, O.J. (1990). *Int. J. Chem. Kinet.* 22, 1111.
- Niki, H., Maker, P.D., Savage, C.M., and Breitenbach, L.P. (1978). *J. Phys. Chem.* 82 132.
- Perry, R.A., Atkinson, R., and Pitts, Jr., J.N. (1977). *J. Chem. Phys.* 67, 611.
- Scollard, D.J., Treacy, J.J., Sidebottom, H.W., Balestra-Garcia, C., Laverdet, G., LeBras, G., MacLeod, H., Teton, S. (1993). *J. Phys. Chem.* 97, 4683.
- Selwyb, G., Podolske, J., Johnston, H. S. (1977). *Geophys. Res. Lett.* 4, 427.
- Semmes, D.H., Ravishankara, A.R., Gump-Perkins, C.A., and Wine, P.H. (1985). *Int. J. Chem. Kinet.* 17, 303.
- Simonaitis, R., and Heicklen, J. (1973). *J. Phys. Chem.* 77, 1932.
- Slagle, I.R. and Gutman, D. (1982). *J. Am. Chem. Soc.* 104, 4741.
- Smith, D.F., Kleindienst, T.E., Hudgens, E.E., McIver, C.D., and Bufalini, J.J. (1991). *Int. J. Chem. Kinet.* 23, 907.
- Tuazon, E.C., Carter, W.P.L., Aschmann, S.M., and Atkinson, R. (1991). *Int. J. Chem. Kinet.* 23, 1003.
- Taylor, P.H., Rahman, M.Sm., Arif, M., Dellinger, B., and Marshall, P.M. (1996). Twenty-Sixth Symp. (Int.) on Comb., in press.
- Tully, F.P. and Droege, A.T. (1987). *Int. J. Chem. Kinet.* 19, 251.
- Tyndall, G.S., Staffelbach, T.A., Orlando, J.J., Calvert, J.G. (1995). *Int. J. Chem. Kinet.* 27, 1009.
- US-EPA. (1988). *Guidance on Estimating Motor Vehicle Emission Reductions from the Use of Alternative Fuels and Fuel Blends*, Report No 1 EPA-AA-TSS-PA-87-4, Ann Arbor, MI.
- Wallington, T.J., Liu, R., Dagaut, P., and Kurylo, M.J. (1988a). *Int. J. Chem. Kinet.* 20, 41.
- Wallington, T.J., Dagaut, P., Liu, R., and Kurylo, M.J. (1988b). *Environ. Sci. Technol.* 22, 842.
- Wallington, T.J., Andino, J.M., Skewes, L.M., Siegl, W.O., and Japar, S.M. (1989). *Int. J. Chem. Kinet.* 21, 993.
- Warnatz, J. (1984). *Combustion Chemistry*, Gardiner, Jr., W.C., Ed., Springer-Verlag: New York, Chap. 5.

Wagman, D.D., Evans, W. H., Parker, V. B., Schumm, R. H., Halow, I., Bailey, S. M., Churney, K. L., Nuttall, R. L. (1982). J. Phys. Chem. Ref. Data 11, Supplement 2.

Westmoreland, P.R., Howard, J.B., Longwell, J.P., and Dean, A.M. (1986). AIChE J. 32, 1971.

REPORT DOCUMENTATION PAGE

Form Approved
OMB NO. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE July 1996	3. REPORT TYPE AND DATES COVERED NREL Subcontractor Report	
4. TITLE AND SUBTITLE The Origin and Fate of Organic Pollutants from the Combustion of Alternative Fuels: Phase III Report		5. FUNDING NUMBERS FU622010	
6. AUTHOR(S) P.H. Taylor, B. Dellinger, M. Rahman			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) UDRI 300 College Park Drive Dayton, OH 45469-0132		8. PERFORMING ORGANIZATION REPORT NUMBER DE96007952	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) National Renewable Energy Laboratory 1617 Cole Boulevard Golden, CO 80401-3393		10. SPONSORING/MONITORING AGENCY REPORT NUMBER NREL/TP-473-21082	
11. SUPPLEMENTARY NOTES			
12a. DISTRIBUTION/AVAILABILITY STATEMENT National Technical Information Service U.S. Department of Commerce 5285 Port Royal Road Springfield, VA 22161		12b. DISTRIBUTION CODE UC-1500	
13. ABSTRACT (Maximum 200 words) The overall objective of this project is to determine the impact of alternative fuels on air quality, particularly ozone formation. This objective will be met through three steps: (1) qualitative identification of alternative fuel combustion products; (2) quantitative measurement of specific emission levels of these products; and (3) determination of the fate of the combustion products in the atmosphere, particularly in terms of depletion or conversion by hydroxyl radical attack. The alternative fuels of interest are methanol, ethanol, natural gas, and liquefied petroleum gas.			
14. SUBJECT TERMS methanol, ethanol, natural gas, liquefied petroleum gas, ozone formation, combustion products		15. NUMBER OF PAGES 22	
		16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18
298-102