TABLE III: Comparison of Measurements and Theoretical Calculations for HO₂ Band Intensities

	6 	and intensit				
ref	$^{\nu_3}$ 1098 cm ⁻¹	$^{\nu_2}$ 1392 cm ⁻¹	$^{\nu_1}_{3436 \text{ cm}^{-1}}$	method		
this work	35 ± 9	58 ± 16	20 ± 6	diode laser-discharge flow		
22	35 ± 13	80 ± 13		diode laser-molecular modulation		
23	30 ± 10			diode laser-flash photolysis		
21		80		low-resolution molecular modulation		
24	(1.4)	(3)	(1)	matrix isolation (relative strengths only)		
8	210	240	300	ab initio calculation		
9	120	350	210	ab initio calculation		
	56	280	90	atomic polar tensor transfer from CH ₃ OH and H ₂ O		

molecular modulation method and obtained an approximate value of ~80 cm⁻² (STP atm)⁻¹ for the ν_2 band. The relative strengths for the three bands are in qualitative agreement with the ratios determined from averaging the optical depths in the matrix isolation spectra of Smith and Andrews.²⁴

The comparison with theoretical calculations is less satisfactory. The calculations of both Komornicki and Jaffe⁸ and of Maia⁹ predict band strengths larger by a factor of 1.6-6 than our experimental values for the ν_2 and ν_3 bands and by up to a factor of 10 for the v_1 band. The calculation that comes closest in both absolute and relative values is the method of transferring atomic polar tensors calculated for similar molecules such as CH₃OH and H_2O .⁹ These computational methods have been more successful for related molecules, such as HOCl.9

The best spectral features for concentration measurements of HO_2 by infrared absorption are the strong coincident line pairs

(24) Smith, D. W.; Andrews, L. J. Chem. Phys. 1974, 60, 81.

in the ν_2 P branch around 1370 cm⁻¹ and in the R branch around 1410 cm⁻¹. This spectral region is also sufficiently free from interferences due to atmospheric trace gases under stratospheric conditions to make long path absorption measurements a future possibility. The line pair at 1371.927 cm⁻¹ has a combined strength of 1.5×10^{-20} cm² molecule⁻¹ cm⁻¹ at 225 K. This corresponds to a fractional absorption at line center of 1.3×10^{-5} over a 1-km path for an expected HO₂ mixing ratio at 30-km altitude of 200 ppt.^{25,26} Since this is just at the detection limit of current balloon-borne instrumentation, 27,28 in situ measurements of HO₂ by infrared absorption will depend on further technological developments.

The strong lines in the v_2 band are sufficient for monitoring HO₂ in laboratory studies of HO₂ reaction kinetics. In our present flow system with an effective multiple-pass path length of 200 cm, a minimum fractional absorption of 10⁻⁵ corresponds to an HO₂ detection limit of 1×10^{10} molecules cm⁻³. While this is sufficient for many laboratory applications, future improvements in diode laser methodology may be expected to further lower this limit.

Acknowledgment. This work has been supported by the National Aeronautics and Space Administration under Contracts NASW-3877 and NASW-4051 and by the Chemical Manufacturers Association under Contract FC-83-469. We are indebted to Dr. A. G. Maki for supplying the computer program for the asymmetric rotor calculations, to Dr. E. Hirota for a complete set of line positions for the v_2 band, and to Drs. James Burkholder and Gary Hayman for communicating their results prior to publication. Dr. Frederick Kaufman provided inspiration and motivation in the early stages of this work. We deeply miss the insight, criticism, and humor he provided as a consultant at Aerodyne.

Registry No. HO₂, 3170-83-0.

- (26) Helten, M.; Patz, W.; Trainer, M.; Fark, H.; Klein, E.; Ehhalt, D. H. J. Atmos. Chem. 1984, 2, 191.
- (27) Menzies, R. T.; Webster, C. R.; Hinkley, E. D. Appl. Opt. 1983, 22, 2655.
 - (28) Webster, C. R.; May, R. D. J. Geophys. Res. 1987, 92, 11931.

Kinetics of the Reactions of $CH_2(\tilde{X}^3B_1)$ Radicals with NO and NO₂

V. Seidler, F. Temps, H. Gg. Wagner,* and M. Wolf

Max-Planck-Institut für Strömungsforschung, Bunsenstrasse 10, 3400 Göttingen, West Germany (Received: January 4, 1988)

The kinetics of the reactions of CH₂ radicals in their triplet electronic ground state (\tilde{X}^3B_1) with NO and NO₂ $[CH_2(\tilde{X}^3B_1)$ + NO \rightarrow products (1); CH₂($\tilde{X}^{3}B_{1}$) + NO₂ \rightarrow products (2)] have been studied at room temperature in isothermal discharge flow systems. CH_2 radicals were generated either by exciplex laser photolysis of CH_2CO or via the reaction $O + CH_2CO$ \rightarrow CH₂ + CO₂. The CH₂ concentration was monitored directly with a far-infrared laser magnetic resonance spectrometer. From the decay of [CH₂] under pseudo-first-order conditions the rate constants of reactions 1 and 2 were obtained to be $k_1(296K) = (2.2 \pm 0.5) \times 10^{13} \text{ cm}^3/(\text{mol s}) \text{ and } k_2(296K) = (5.9 \pm 1.4) \times 10^{13} \text{ cm}^3/(\text{mol s}).$

Introduction

The formation and consumption of nitric oxides, NO₂, in flames have long been an outstanding research topic in reaction kinetics and combustion science.

Several NO_x sources have now been well established.¹⁻³ The

combustion of fuel N can be described by the overall scheme

fuel N
$$\rightarrow$$
 HCN \rightarrow NCO \rightarrow NH, (*i* = 1, 2)

given by Haynes.^{1,2} Atmospheric N₂ may be converted to NO_x via the so-called Zeldovich mechanism.³ Eventually, reactions between N₂ and small hydrocarbon radicals, e.g., CH or CH₂,

⁽²⁵⁾ Anderson, J. G.; Grassl, H. J.; Shetter, R. E.; Margitan, J. J. Geophys. Res. Lett. 1981, 8, 289.

 ⁽¹⁾ Haynes, B. S. Combust. Flame 1977, 28, 81.
 (2) Haynes, B. S. Combust. Flame 1977, 28, 113.

⁽³⁾ Fenimore, C. B. 13th Symposium (International) on Combustion; The Combustion Institute: Pittsburgh, 1970.

lead to the so-called "prompt" NO formation.³

On the other hand, there are only few reaction channels to consume NO_x. A comparison of the rates and products of reactions of the most important free radicals with NO on the one side and O_2 and, as a representative fuel, H_2 on the other side⁴⁻⁶ reveals that the reaction⁷ of NO with NH₂ is by far the single most important pathway for the direct reduction of NO to N_2 . As a consequence, both the $DeNO_x$ and the RAPRENO_x processes^{8,9} depend on the presence of NH₂, which is generated by adding either NH₃⁸ or HNCO⁹ as NH₂ precursors.

Besides these direct NO_x reduction methods, which in practice are usually applied to the post-flame gases, there are important other "natural" NO_x destruction pathways that have to be taken into account in modeling NO_x . Such channels can arise through the reactions of small hydrocarbon radicals, e.g., CH, CH₂, or, possibly, CH₃ with NO, which reintroduce NO_x into the reaction cycle of the Haynes mechanism by regenerating the (NCO) or (CN) structural units. Thus, once formed, NO may lead to the reformation of NH_i radicals (i = 1, 2) which then effectively convert NO to N₂.

In particular, the role of methylene radicals, CH_2 , in their triplet electronic ground state (\tilde{X}^3B_1) is of interest.¹⁰⁻¹² CH₂ radicals are known to be produced in combustion processes in high concentrations. The reactions of CH_2 with NO and NO_2

$$CH_2(\tilde{X}^3B_1) + NO \rightarrow \text{products}$$
 (1)

$$CH_2(\tilde{X}^3B_1) + NO_2 \rightarrow products$$
 (2)

can provide a pathway for regenerating the (NCO) or (CN) units. Hence, reliable information on the kinetics of both these reactions is of importance for the modeling of combustion processes.

In addition to this more applied point of view, the mechanisms of reactions 1 and 2 are of considerable interest due to their nature as radical-radical reactions. The reactions may lead to a variety of products that can arise through a sequence of unimolecular isomerization and fragmentation reactions of the initially formed short-lived highly vibrationally excited addition complexes. Understanding of the complicated rearrangement processes of the atoms involved presents a challenge to both ab initio quantum chemical methods and unimolecular rate theory.

It has been the task of the present work to study the kinetics of reactions 1 and 2. The investigations have been carried out in the gas phase by using the discharge flow technique in connection with far-infrared laser magnetic resonance (LMR) detection of $CH_2(\tilde{X}^3B_1)$. A study of the product distribution will be reported in a subsequent publication.

Experimental Section

The reactions have been investigated at room temperature in an isothermal discharge flow system. The experimental setup has been described in detail earlier.¹³ The flow reactor consisted of a 4.0-cm-i.d. Pyrex tube coated with a thin film of Teflon (Du Pont FEP 856-200) and equipped with a movable probe. A 15-cm-long photolysis cell was attached to the main tube at its



Figure 1. Typical semilogarithmic CH2 decay plots measured for reaction 1 at four different NO concentrations.

upper end for the generation of radicals by exciplex laser photolysis of a precursor.

The flow system was connected to a far-IR LMR spectrometer¹³ for the detection of radicals. $CH_2(\tilde{X}^3B_1)$ was monitored at $\lambda =$ 158 μ m (¹³CH₃OH), $B_0 = 0.323$ T with π -polarization.¹⁴ O atoms were observed via their vacuum ultraviolet resonance absorption.

Helium served as the main carrier gas. All gases used were of the highest commercially available purities (He, 99.9999%; Ar, 99.9999%; O2, 99.998% (2% premixed in He); H2, 99.9999%; NO, 98.5%; NO₂, 99.5%; all Messer Griesheim). He and O₂ were further purified by using $N_2(1)$ traps. NO was purified by passing it first through a KOH tower and then through an acetone/dry ice trap. Ketene was prepared by pyrolysis of acetone and purified by repeated trap-to-trap distillation.

CH₂ radicals were generated in two different sources which have been described in detail before.^{10,12} The first method employed exciplex laser photolysis of CH₂CO at $\lambda = 193$ nm:^{12,15}

$$CH_2CO + h\nu \rightarrow CH_2 + CO$$
 (3)

An estimate of the initial CH₂ concentration was obtained by comparing the CH₂ LMR signals from CH₂CO photolysis at λ = 308 and 193 nm and using the known absorption coefficient at the former wavelength.¹⁵ The second source was the reaction of oxygen atoms with ketene:^{10,16}

$$O + CH_2CO \rightarrow CH_2 + CO_2 \tag{4a}$$

$$\rightarrow$$
 other products (4b)

which also served for the determination of absolute CH₂ concentrations. The branching ratio for the main channel (4a) has recently been measured in an independent investigation¹⁷ to be $k_{4a}/k_4 = 0.85 \pm 0.15$. Absolute O-atom concentrations were determined by using the well-known titration reaction N + NO \rightarrow N₂ + O.¹⁸

Results

The rate constants of reactions 1 and 2 were determined by monitoring the CH₂ concentration along the reaction distance in the absence and in the presence of a large excess of NO or NO_2 , respectively. The rate constant for the small contribution to the CH₂ decay due to the heterogeneous reaction

$$CH_2 + wall \rightarrow products$$
 (5)

was measured directly in the absence of the reactants by using

⁽⁴⁾ Warnatz, J. In Combustion Chemistry; Gardiner, W. C., Ed.; Springer: New York, 1984

⁽⁵⁾ Hanson, R. K.; Salimian, S. In Combustion Chemistry; Gardiner, W. C., Ed.; Springer: New York, 1984.
(6) Seidler, V. Diploma Thesis, Göttingen, 1986.

⁽⁷⁾ Gehring, M. Ph.D. Thesis, Göttingen, 1971. Gehring, M.; Hoyermann, K.; Schacke, H.; Wolfrum, J. 14th Symposium (International) on Combus-

tion; The Combustion Institute: Pittsburgh, 1973. (8) Dean, A. M.; Hardy, J. E.; Lyon, R. K. 19th Symposium (Interna-

⁽i) Dean Combustion; The Combustion Institute: Pittsburgh, 1982.
(9) Perry, R. A.; Siebers, D. L. Nature (London) 1986, 324, 657.
(10) Böhland, T.; Temps, F.; Wagner, H. Gg. Ber. Bunsen-Ges. Phys. Chem. 1984, 88, 455.

⁽¹¹⁾ Böhland, T.; Temps, F.; Wagner, H. Gg. 21st Symposium (International) on Combustion; The Combustion Institue: Pittsburgh, 1986; p 841.

⁽¹²⁾ Böhland, T.; Temps, F.; Wagner, H. Gg. J. Phys. Chem. 1987, 91, 1205.

⁽¹³⁾ Böhland, T.; Temps, F.; Wagner, H. Gg. Z. Phys. Chem. (Neue Folge) 1984, 142, 129.

⁽¹⁴⁾ Sears, T. J.; Bunker, P. R.; McKellar, A. R. W.; Evenson, K. M.; Jennings, D. A.; Brown, J. M. J. Chem. Phys. 1982, 77, 5348

⁽¹⁵⁾ Okabe, H. Photochemistry of Small Molecules; Wiley: New York, 1978.

⁽¹⁶⁾ Washida, N.; Hatakeyama, S.; Takagi, H.; Kyogoku, T.; Sato, S. J. Chem. Phys. 1983, 78, 4533.

⁽¹⁷⁾ Koch, M.; Bley, U.; Temps, F.; Wagner, H. Gg., to be submitted for publication.

⁽¹⁸⁾ Kaufman, F.; Kelso, J. R. 7th Symposium (International) on Combustion; The Combustion Institute; Butterworths: London, 1959. Kaufman, F. Prog. React. Kinet. 1961, 1, 1.

TABLE I: Experimental Results for the Reaction $CH_2 + NO(1)$

p, mbar	<i>v</i> , ms ⁻¹	10 ¹¹ [CH ₂ CO], mol cm ⁻³	$10^{12}[O_2]_{0}^{a}$ mol cm ⁻³	10 ¹² [NO], mol cm ⁻³	$k_1[NO], s^{-1}$	$10^{-13}k_1,$ cm ³ mol ⁻¹ s ⁻¹	
1.36	13.0	15.8	0	2.0	41	2.1	
2.95	20.3	11.1	0	2.6	58	2.2	
1.39	18.8	51.4	1.4	2.9	78	2.7	
1.33	29.8	9.4	0	3.2	80	2.5	
1.39	18.8	45.0	1.4	5.0	120	2.4	
1.92	12.6	50.2	2.1	7.4	189	2.6	
1.39	18.8	45.0	1.4	7.5	167	2.2	
1.53	39.6	4.5	0	7.6	175	2.3	
1.40	34.0	39.0	1.9	8.7	180	2.1	
1.53	39.6	4.5	0	10.1	263	2.6	
1.51	39.7	5.6	0	12.2	246	2.0	
1.53	39.4	4.6	0	16.3	368	2.3	

^{*a*} For $[O_2]_0 = 0$ the CH₂ source (3) was used.

TABLE II: Experimental Results for the Reaction $CH_2 + NO_2$ (2)

p, mbar	<i>v</i> , ms ⁻¹	10 ¹¹ [CH ₂ CO], mol cm ⁻³	$10^{12}[O_2]_{0,a}$ mol cm ⁻³	$10^{12}[NO_2],$ mol cm ⁻³	$k_2[NO_2], s^{-1}$	$10^{-13}k_2,$ cm ³ mol ⁻¹ s ⁻¹
2.73	24.6	67.0	0	0.64	38	5.6
1.56	38.2	5.2	0	1.63	86	5.3
2.83	13.5	12.0	0	1.90	84	4.4
1.88	25.3	43.1	2.5	2.42	138	5.7
1.40	34.0	31.7	1.8	3.61	183	5.1
1.52	39.4	7.0	0	4.09	244	6.2
1.51	39.8	4.1	0	6.17	372	6.0
1.40	34.0	24.0	1.8	6.28	343	5.5

^{*a*} For $[O_2]_0 = 0$ the CH₂ source (3) was used.

low initial radical concentrations, $[CH_2]_0 \le 5 \times 10^{-14} \text{ mol/cm}^3$, yielding $k_5 \approx 15 \text{ s}^{-1}$.

In the presence of the reactants, reactions 1 and 2, respectively, constitute the main CH₂ depletion pathways. Reactions of CH₂ with the products of (1) and (2) can be neglected for $[CH_2]_0 \ll k_1[NO]/k_{P1}$ and $[CH_2]_0 \ll k_2[NO_2]/k_{P2}$, where k_{P1} and k_{P2} are the rate constants for reactions of CH₂ with products from (1) and (2), respectively. The combination reaction CH₂ + CH₂ \rightarrow C₂H₂ + 2H cannot play a significant role for $[CH_2] < 10^{-13}$ mol/cm³.

Figure 1 shows some typical semilogarithmic CH_2 decay plots for reaction 1 at four different reactant concentrations. The CH_2 depletion was followed over more than one order of magnitude change in concentration. Over this range, the semilogarithmic decay plots were strictly linear, indicating the validity of pseudo-first-order behavior.

The experimental results are summarized in Tables I and II. The reactions were studied at pressures between 1.3 mbar $\leq p \leq 3.6$ mbar and at flow velocities of 12 m/s $\leq v \leq 40$ m/s. Initial CH₂ concentrations were in the regime 2 × 10⁻¹⁴ mol/cm³ \leq [CH₂]₀ \leq 1 × 10⁻¹³ mol/cm³. The reactant concentrations were varied between 2 × 10⁻¹² mol/cm³ \leq [NO₂] \leq 2 × 10⁻¹¹ mol/cm³. The reactant excess ratios were 40 \leq [NO]/[CH₂]₀ \leq 2000 and 5 \leq [NO₂]/[CH₂]₀ \leq 200, where, however, the lowest value of 5 refers only to the first entry in Table II. Thus, even with k_{P1} , $k_{P2} \simeq 10^{14}$ cm³/(mol s) close to the gas kinetic collision frequency, consecutive reactions cannot play a role.

Figures 2 and 3 show the measured pseudo-first-order rate constants plotted versus [NO] and [NO₂], respectively. The data points are described by straight lines through the origin. A least-squares fit yields $k_1(296K) = (2.2 \pm 0.2) \times 10^{13} \text{ cm}^3/(\text{mol s})$ and $k_2(296K) = (5.9 \pm 0.7) \times 10^{13} \text{ cm}^3/(\text{mol s})$, where the error limits correspond to the 95% confidence interval.

Discussion

The present investigation of reactions 1 and 2 has been carried out by using two different CH₂ radical sources. The results obtained show very good agreement. The small intercepts of k'_1 = $8 \pm 21 \text{ s}^{-1}$ and $k'_2 = -11 \pm 25 \text{ s}^{-1}$ in Figures 2 and 3 are not believed to be of significance, since the values are smaller than the 2σ standard deviations. With inclusion of estimated system-



Figure 2. Pseudo-first-order rate constants for reaction 1 as a function of the NO concentration.



Figure 3. Pseudo-first-order rate constants for reaction 2 as a function of the NO_2 concentration.

atical errors the final results for the rate constants of reactions 1 and 2 at room temperature are

Reactions of $CH_2(\tilde{X}^3B_1)$ Radicals with NO and NO₂

$$k_1(296\text{K}) = (2.2 \pm 0.5) \times 10^{13} \text{ cm}^3/(\text{mol s})$$

 $k_2(296\text{K}) = (5.9 \pm 1.4) \times 10^{13} \text{ cm}^3/(\text{mol s})$

Previous determinations of k_1 have been carried out with indirect techniques. The results depend strongly on details of the adopted reaction mechanisms. Laufer and Bass measured the yields of C_2H_2 in the photolysis of $CH_2CO/He/NO$ mixtures and obtained a value of $k_1 = 9.6 \times 10^{12}$ cm³/(mol s).¹⁹ Similarly, Pilling and Robertson found values around $k_1 = 6 \times 10^{12}$ cm³/(mol s).²⁰ Their results also suggested the existence of a weak pressure dependence of k_1 . Vinckier and Debruyn investigated the fate of CH₂ radicals produced in the reaction of O atoms with C_2H_2 in a flow system.²¹ From the steady-state CH₂ concentration measured mass spectrometrically they deduced a room-temperature rate constant of $k_1 = 8.8 \times 10^{12}$ cm³/(mol s). These indirect values are lower than the result of the direct study described here by factors of 2–4. Measurements of the rate constant for reaction 2 have not yet been reported to our knowledge.

As is generally expected for radical-radical reactions, both (1) and (2) exhibit very high rate constants close to the gas kinetic collision frequencies. For comparison, the calculated Lennard-Jones collision frequencies²² are $Z_{LJ,1} = 2.0 \times 10^{14} \text{ cm}^3/(\text{mol s})$ and $Z_{LJ,2} = 2.5 \times 10^{14} \text{ cm}^3/(\text{mol s})$.

The data for reaction 1 can also be compared to the corresponding reaction of CH₂ in its singlet first excited electronic state $(\tilde{a}^{1}A_{1})$, which has a 4 times larger total rate constant, $k = 9.6 \times 10^{13} \text{ cm}^{3}/(\text{mol s}).^{23}$

Concerning the reaction mechanisms and products, as radical-radical reactions both (1) and (2) are expected to proceed via recombination to form the highly vibrationally excited intermediates CH_2NO^* and CH_2ONO^* or $CH_2NO_2^*$, respectively. The initial complex-forming steps are highly exothermic:

 $CH_2 + NO \rightarrow CH_2NO$ $\Delta H_R^{\circ}_{298} = -307 \text{ kJ/mol}$ (1a)

$$CH_2 + NO_2 \rightarrow CH_2ONO \qquad \Delta H_R^{\circ}_{298} = -277 \text{ kJ/mol} \quad (2b)$$

 $CH_2 + NO_2 \rightarrow CH_2NO_2 \qquad \Delta H_R^{\circ}_{298} = -276 \text{ kJ/mol} \quad (2b)$

Under the conditions used in this study, the recombinations to stable CH_2NO , CH_2ONO , or CH_2NO_2 are expected to be in the low-pressure regime. Their rate constants should be several orders of magnitude smaller than the measured values. Thus, collisional stabilization cannot play a significant role here. Instead, the measured very high rate constants of reactions 1 and 2 indicate that the highly vibrationally excited intermediates undergo, possibly after prior isomerization, very fast unimolecular fragmentation reactions.

Possible product channels for reaction 1 are illustrated in Figure 4. The thermodynamic heats of formation of the species involved were taken from the tables of Melius.²⁴ Of the different products, the radicals OH, HCO, NH, and NH₂ as well as CN can in



Figure 4. Energy diagram for possible products of reaction 1. Thermodynamic heats of formation of the different species have been taken from ref 24.

principle be detected with the LMR, and H, N, or O are detectable with the ESR. A preliminary investigation showed that neither OH nor H atoms are main products ($\leq 10\%$ OH, $\leq 10\%$ H). It should be noted that a straightforward C-H bond rupture in CH₂NO leading to H + HCNO is energetically unfavorable, since the HCNO formed would be a diradical. On the other hand, according to the quantum chemical calculations,²⁴ the isomerization of CH₂NO to HCNOH, which must proceed a dissociation to form OH + HCN, is possible only via a very high, energetically just allowed barrier. The absence of large OH product concentrations then seems to indicate the existence of another, lower energy isomerization pathway, e.g., to a (NCO) or (CNO) type structure.

A plausible fragmentation channel for the CH₂ONO* formed in reaction 2 would be the production of CH₂O + NO. Dissociation of CH₂NO₂* to CH₂NO + O cannot account for more than 20% of the overall reaction, since the O atoms would lead to a regeneration of CH₂ via (4), which was not observed to be significant.

An elucidation of the detailed mechanisms of both reactions 1 and 2 requires further experimental and theoretical studies, which are under way and will be reported in a subsequent publication.

Acknowledgment. We thank the Fond der Chemie for support of this work and Dr. C. Melius for providing a copy of his results prior to publication.

Registry No. CH₂, 2465-56-7; NO, 10102-43-9; NO₂, 10102-44-0; CH₂CO, 463-51-4.

⁽¹⁹⁾ Laufer, A. H.; Bass, A. M. J. Phys. Chem. 1974, 78, 1344.

⁽²⁰⁾ Pilling, M. J.; Robertson, J. A. J. Chem. Soc., Faraday Trans. 1 1977, 73, 968.

⁽²¹⁾ Vinckier, C.; Debruyn, W. J. Phys. Chem. 1979, 16, 2057. (22) Hirschfelder, J. O.; Curtiss, C. F.; Bird, R. B. Molecular Theory of Gases and Liquids; Wiley: New York, 1954.

⁽²³⁾ Langford, A. O.; Petek, H.; Moore, C. B. J. Chem. Phys. 1983, 78, 1983.

⁽²⁴⁾ Melius, C. F., private communication.