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A Resonance-Fluorescence Kinetic Study
of Oxygen Atom + Hydrocarbon Reactions, V:
 $O(^3P) + \text{Neopentane}$ (415-922K)

MASTER

by

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ABSTRACT

Absolute values of the rate constants for the reaction of $O(^3P)$ with neo- C_5H_{12} were determined directly with the use of the complementary techniques: flash photolysis (FP) and discharge flow (DF). The O-atoms were monitored via resonance fluorescence (RF) in both systems, allowing experiments to be carried out at very low $[O]$. Secondary reactions were averted in this way, and the rate data thus obtained were stoichiometry-free. The DF-RF experiments were performed over the temperature range, 427-922K while those with the FP-RF apparatus were performed from 415-528K. Over the common range of temperature the absolute rate constants were in excellent agreement. The combined set of data from 415-922K is well described by $k_1 = (1.52 \pm 0.28) \times 10^{-10} \exp(-7143 \pm 196/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ where R is expressed in $\text{cal mole}^{-1} \text{ K}^{-1}$ and the errors are taken at the two standard deviation level (95% confidence). The bond energy-bond order (BEBO) method along with activated complex theory was applied to the title reaction, and satisfactory agreement with experimental rate constants was obtained.

INTRODUCTION

Increasing interest in hydrocarbon combustion has prompted renewed work on chemical mechanisms for high temperature hydrocarbon oxidation.^{1,2} In the past two to three years, several $O(^3P) + RH$ reaction rate constants have been determined in this laboratory over substantial ranges of temperature (~400-1100K) in an attempt to further define the rate behavior for application in high temperature combustion. In this paper we give results for the reaction,

To date there have been only two absolute reaction rate studies of reaction (1). Wright³ obtained a value of $3.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 303K. Herron and Huie⁴ report the only temperature dependent study: $k_1 = (1.0 \pm 0.4) \times 10^{-10} \exp(-5802 \pm 278/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (here and throughout the paper R is expressed in $\text{cal mole}^{-1} \text{ K}^{-1}$). They have determined the rate behavior from 276-597K by means of the discharge flow-mass spectrometric (DF-MS) technique. The work was performed under excess [O] conditions, and the attenuation of neo-C₅H₁₂ as a function of distance (time) was measured. Using this procedure they assumed the system to be free from stoichiometric corrections because it is unlikely that the parent hydrocarbon could be reformed by any process or could react competitively with reaction products. However, the Herron and Huie study required an accurate knowledge of absolute [O] for precise absolute k_1 determination.

The present study was carried out with two well known methods both of which utilize atomic resonance fluorescence detection of $O(^3P)$. These are flash photolysis-resonance fluorescence (FP-RF) and discharge flow-resonance fluorescence (DF-RF). With both techniques [O] attenuation as a function of time is measured in the presence of excess neo-C₅H₁₂. However, the detection technique is sufficiently sensitive that secondary depletion of atoms by homogeneous reaction with products is not significant. Indeed, experiments are performed to show this, thus demonstrating that the present results are free from stoichiometric corrections. We present results from measurements over the range in temperature of 415-922K. The primary goal of this study is to compare the present results with those of Herron and Huie,⁴ particularly over the common range of temperature in the two studies. In addition, the results of a theoretical calculation using the BEBO-ACT method are presented.

EXPERIMENTAL

The rate constant for reaction (1) was studied by two direct and complementary techniques: (1) Flash Photolysis-Resonance Fluorescence (FP-RF);^{5,6} and (2) Discharge Flow-Resonance Fluorescence (DF-RF).^{7,8} Both techniques have been utilized in this laboratory in previous investigations,⁸⁻¹⁰ so only a brief description will be given here.

The FP-RF apparatus was used for rate measurements at five temperatures ranging from 415 to 528K. The photodecomposition of O₂ with $\lambda > 160$ nm (suprasil cutoff) served as the source of O-atoms. With this wavelength discrimination, the photodecomposition of the reactant, neo-C₅H₁₂, was minimized. Pre-formed mixtures of buffer gas (80% Ar and 20% N₂) and O₂ along with variable amounts of neo-C₅H₁₂ were flowed slowly (~ 1 -5 cm s⁻¹) through the reaction cell. This procedure replenished the cell contents between photo flashes, and therefore, no reaction product was allowed to build to levels sufficient to perturb the temporal profile of O-atoms. Also the presence of N₂ served to rapidly deactivate the photolysis product, O(¹D), to ground state O(³P) atoms.¹⁰

The DF-RF apparatus was used for rate measurements from 427 to 922K, so the range of temperature overlap between the two techniques is substantial. O-atoms were generated upstream from the thermostated flow reactor by passing O₂ diluted in the He carrier gas through a microwave discharge. Alternatively, atomic oxygen was generated by titrating N-atoms, produced from N₂, with NO which was also introduced upstream from the flow reactor but downstream from the discharge. The latter procedure allowed for precise calibration, and also, when the NO was introduced through the movable probe, for the determination of the rate constant for wall destruction of O-atoms. After flow tube treatment with dilute HF, typical values of $k_w = 5$ s⁻¹ were readily obtained at any temperature. The sensitivity for detection of O atoms is about 10⁹ atoms cm⁻³ at a signal to noise ratio of one. Most experiments were performed with $5 \times 10^{10} \leq [O]_0 \leq 1 \times 10^{12}$ atoms cm⁻³.

Neo-C₅H₁₂ was obtained from the API Research Project 588 (Carnegie-Mellon University) and was of greater than 99.997% purity. Gas chromatographic analysis revealed no detectable impurities, so the API purity certification is conservative. All other reagents except NO were of research grade and were used without further purification. O₂ was MG Scientific (99.995%); He, Ar, and N₂ were from Matheson (99.9999%, 99.9995%, and 99.9995%, respectively). NO was obtained from Matheson (99.0% purity) and was outgassed and vacuum distilled from 90 to 77K before use. Only the middle one third was retained.

RESULTS AND DISCUSSION

Since resonance fluorescence is such a sensitive technique, it was possible to perform all experiments under pseudo-first-order conditions. With either apparatus the $[\text{neo-C}_5\text{H}_{12}]/[\text{O}]_0$ ratios were always greater than 200. Therefore, with reaction (1) as the only removal process, O-atoms are expected to exhibit a logarithmic decay, as a function of reaction time, that is linearly dependent on $k_1[\text{neo-C}_5\text{H}_{12}]$. However, before such an assertion can be made, other processes that could possibly perturb $[\text{O}]$ have to be ruled out.

In the present case, impurity levels are too low to cause significant perturbations. Also, as noted earlier, no products accumulate, and therefore, the only possible perturbing influences on $[\text{O}]$ are the initially formed radicals from the photoflash (FP-RF experiment), the wall reaction (DF-RF experiment), or primary products from reaction (1) (both FP-RF and DF-RF experiments). The last possibility can be assessed by utilizing variable $[\text{O}]_0$ in otherwise identical experiments. This is accomplished in the FP-RF experiment with variable flash energy and in the DF-RF experiment by discharging larger concentrations of O_2 (or $\text{N}_2 + \text{NO}$).

Initial experiments with the FP-RF apparatus revealed a small but detectable flash energy effect particularly at $T < 458\text{K}$. For example a definite increase in the first order decay constant at 458K was noted at flash energies greater than 40 J. Similar behavior was noted at the other temperatures, and therefore, care was taken to establish the lower range of flash energies over which no variation, outside experimental error, occurred. Under these low flash energy conditions, the depletion of $[\text{O}]$ is then given by:

$$\ln([\text{O}]_t/[\text{O}]_0) = -Kt, \quad (1)$$

where $[\text{O}]_t$ and $[\text{O}]_0$ are the O atom concentrations at time = t and time = 0, respectively, and are proportional to fluorescence counts. K is the experimental first-order decay constant and is determined from linear least squares analysis of the logarithm of fluorescence counts against time. Even with no secondary complications, K is still a composite since atoms can be removed by three processes: reaction (1); termolecular recombination with O_2 ; and diffusion out of the viewing zone which is determined by the intersection volume of the photoflash, resonance lamp beam, and detector solid angle. The latter two loss terms were determined simultaneously (as K') and directly in experiments where $[\text{neo-C}_5\text{H}_{12}] = 0$. Thus,

$$K' = k_r[O_2][M] + K_{\text{diffusion}}, \quad (\text{II})$$

and then,

$$K = k_1[\text{neo-C}_5\text{H}_{12}] + K'. \quad (\text{III})$$

The bimolecular rate constant for reaction (1) can then be calculated by rearrangement of Eq. (III),

$$k_1 = (K - K')/[\text{neo-C}_5\text{H}_{12}]. \quad (\text{IV})$$

Table I lists the individual values of K , K' , and the derived k_1 values at five temperatures ranging from 415–528K. Since these results were obtained under limiting low photoflash energies and with flows which were sufficient to replenish the cell contents between flashes, we assert that secondary complications were not contributing. The derived bimolecular rate constants then refer only to reaction (1). The temperature dependence of these results from linear least squares analysis at the one standard deviation level is, $k_1 = (1.78 \pm 0.69) \times 10^{-10} \exp(-7268 \pm 302/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$.

Initial experiments with the DF-RF apparatus also revealed decay constant sensitivity to $[O]_0$. The results were strikingly similar to those found in the FP-RF experiments. Typical results are shown in Fig. 1 where the apparent bimolecular rate constant is plotted against the logarithm of $[O]_0$. At $[O]_0 \sim 10^{12} \text{ atoms cm}^{-3}$ the apparent bimolecular rate constant is higher than the unperturbed value by more than a factor of two. Also distinct non-linearities in first-order plots were noted for these high $[O]_0$ experiments. This behavior clearly supports the FP-RF results and suggests that a fast secondary reaction between O-atoms and a product radical from reaction (1) can become important at high $[O]_0$. Whatever that reaction may be, its perturbing effect can clearly be eliminated at $[O]_0 \sim 5 \times 10^{10} \text{ atoms cm}^{-3}$. Similar experiments at each temperature established the $[O]_0$ upper limit that could be used before secondary complications became significant. All experiments were then carried out under these low $[O]_0$ conditions.

Depletion of $[O]$ can then be attributed to reaction (1) and wall reaction in the DF-RF experiments. The kinetics obey a pseudo-first-order rate law and the temporal behavior of $[O]$ is given by,

$$\ln[O]_d = -k_{obs}(d/v) + \ln[O]_0, \quad (V)$$

where $[O]_d$ and $[O]_0$ are proportional to fluorescence counts, d is the distance from the reactant inlet to the detector, and v is the linear flow velocity. The experimental first-order decay constant, k_{obs} , was obtained by linear least squares analyses of first-order plots according to Eq. (V). The diffusion corrected first-order constant, k_c , was then calculated by the equation,

$$k_c = k_{obs}(1 + k_{obs}D/v^2), \quad (VI)$$

where D is the diffusion coefficient for O-atoms in He.^{8,10} Generally the maximum correction amounted to less than ~15%. Then k_c is related to k_1 through

$$k_c = k_1[\text{neo-C}_5\text{H}_{12}] + \Delta k_w, \quad (VII)$$

where Δk_w is the difference between wall termination constants for O-atom removal with and without added neo-C₅H₁₂. The bimolecular rate constant, k_1 , was determined from linear least squares analyses of the data according to Eq. (VII), and the results are given in Table II.

Three determinations of k_1 were made with the "ON/OFF" method originally described by Westenberg and deHaas.¹¹ With this method the attenuation of $[O]$ is given by

$$\ln([O]_d/[O]_d^0) = -k_{obs}(d/v) \quad (VIII)$$

where $[O]_d^0$ and $[O]_d$ (both proportional to fluorescence counts) are measured at probe distance, d , without and with neo-C₅H₁₂ being present, respectively. The method eliminates the wall reaction process from the analysis. Examples of data plotted according to Eq. (VIII) are given in Fig. 2 where strict first-order behavior is noted over one and a half to three decay lifetimes. The observed first-order decay constants are obtained from linear least squares analyses of such plots, and the resulting values are corrected for diffusion according to Eq. (VI). The k_c values are then plotted against $[\text{neo-C}_5\text{H}_{12}]$ as shown in Fig. 3, and the linear least squares slope is then k_1 since,

$$k_c = k_1[\text{neo-C}_5\text{H}_{12}].$$

(IX)

The $T = 689\text{K}$ "ON/OFF" results are shown specifically in Fig. 3 along with other results which were obtained by means of Eq. (VII). The reason for the comparison between the "ON/OFF" method and that described by Eq. (VII) is to experimentally show the unimportance of the wall reaction process in comparison to reaction (1). This is demonstrated further in Table II where nearly all linear least squares intercepts, Δk_w , are within two standard deviations (95% confidence) of zero regardless of the method of analysis, Eq. (VII) or Eq. (IX). The low wall activity indicated by these reaction experiments corroborates our direct measurement of $k_w \sim 5 \text{ s}^{-1}$. In addition to variations of $[O]_0$, the effects of variable O_2 were examined. O_2 free experiments were carried out with the $N + NO$ titration technique. No effects of O_2 could be documented (outside of experimental error) if $[O]_0$ was maintained at less than $\sim 5 \times 10^{10} \text{ atoms cm}^{-3}$. We therefore assert that the values of the bimolecular rate constants in Table II refer to reaction (1). The temperature dependence of these results from linear least squares analysis at the one standard deviation level is, $k_1 = (1.56 \pm 0.18) \times 10^{-10} \exp(-7191 \pm 135/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

A comparison between the Arrhenius parameters from the present FP-RF and DF-RF results, even at the one standard deviation level, shows virtually exact agreement. Both sets of data can then be taken as one, and, as shown in Fig. 4, the combined results exhibit good linearity on the Arrhenius plot from 415-922K. On linear least squares analysis, the combined results give the Arrhenius expression, $k_1 = (1.52 \pm 0.28) \times 10^{-10} \exp(-7143 \pm 196/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This result has the errors expressed at the two standard deviation level (95% confidence).

Also shown in Fig. 4 are the two results from the only other studies of reaction (1).^{3,4} Wright³ obtained a value of $3.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 303K. This result is shown as the single point in the Figure. The present result extrapolated to 303K would give about one third of Wright's value, $1 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The present results are also lower than those of Herron and Huie.⁴ They report $k_1 = (1.0 \pm 0.4) \times 10^{-10} \exp(-5802 \pm 278/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

This expression is shown as the solid line between two points which define the temperature limits of the previous study. Clearly their A factor is statistically indistinguishable from the present value. The different rate behavior is attributable entirely to a lower activation energy than the one measured in the present work. The

inferred discrepancy at their lowest temperature (276K) with the present Arrhenius parameters would appear to be quite large, the present inference being only 0.13 of their measurement. But the comparison should properly be made over the same range of temperature. At our lower T limit, 415K, our value is 0.3 times theirs, and at their high T limit, 597K, our value is 0.5 times theirs. This comparison shows a discrepancy that is outside the combined errors of both studies and therefore appears to be real. The reasons for it are not at all clear since, as mentioned in the Introduction, the Herron and Huie study should have been free from stoichiometric corrections. However, we emphasize that the results of the present study were also stoichiometry free and that this condition was experimentally demonstrated here. In addition, two different and complementary methods were used in determining absolute values for $k_1(T)$, and a wider range in temperature was covered here than in any previous study. These points therefore suggest a high degree of confidence in the present results.

In addition to the thermal rate studies, the present results may be compared to the molecular beam results of Andresen and Luntz¹² who obtained a threshold energy, E_0 , for reaction (1) of 6.2 kcal mole⁻¹. In deriving this result, they used the excitation functional form, $\sigma \propto (E_c - E_0)$, where E_c is the relative collision energy. With well developed models which relate threshold energies to activation energies,¹³ we calculate for $E_0 = 6.2$ kcal mole⁻¹ an activation energy varying from 6.8 to 7.8 kcal mole⁻¹ for temperatures 400K-900K, respectively. The thermal value from the present study, 7.14 kcal mole⁻¹, for 415K - 922K, is in excellent agreement. Luntz and Andresen¹⁴ have performed theoretical calculations (LEPS) with an assumed three atom model for the intermediate configuration. The potential barrier for reaction (1) was 7.5 kcal mole⁻¹ which implies, on zero point energy correction, an activation energy of 6.5 kcal mole⁻¹. This is lower than measured here, and if an activated complex theory calculation is used, then the implied activation energy to be compared to experiment would be even lower since the theoretical A factor would exhibit some T dependence.

We have also performed theoretical calculations with the BEBO method¹⁵ for determining the activated complex configuration. The method has been applied to $O+CH_4$ and O with several other saturated hydrocarbons including neo-C₅H₁₂. Activated complex theory calculations of the rate constants are then carried out. Full details of these calculations are given elsewhere.¹⁶ The method predicts a potential energy of activation for reaction (1) of 8.21 kcal mole⁻¹. Tunneling factors were included. The only arbitrariness in

these calculations is in the barrier for internal rotation of the complex. Best agreement with experiment was obtained with the assumption of free rotation in the complex. Since there is T dependence from several sources in the pre-exponential factor, the computed rate constants exhibit curvature in an Arrhenius plot. The calculated values are generally larger than experiment being 1.8 times larger at 500K and 1.2 times larger at 900K. The near success of the method particularly at 900K is encouraging because it may provide a rational means for extrapolating the rate constant to the combustion temperature regime.

REFERENCES

1. W. C. Gardiner and D. B. Olson, *Ann. Rev. of Phys. Chem.* 31, 377 (1980).
2. C. K. Westbrook and F. L. Dryer, Eighteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA, 18, 749 (1981).
3. F. J. Wright, Tenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA, 10, 387 (1965).
4. J. T. Herron and R. E. Huie, *J. Phys. Chem.* 73, 3327 (1969).
5. W. Braun and M. Lenzi, *Chem. Soc. Faraday Discuss.* 44, 252 (1967).
6. R. B. Klemm and L. J. Stief, *J. Chem. Phys.* 61, 4900 (1974), and references therein.
7. J. V. Michael and J. H. Lee, *Chem. Phys. Lett.* 51, 303 (1977).
8. R. B. Klemm, E. G. Skolnik and J. V. Michael, *J. Chem. Phys.* 72, 1256 (1980).
9. R. B. Klemm, *J. Chem. Phys.* 71, 1987 (1979).
10. R. B. Klemm, T. Tanzawa, E. G. Skolnik and J. V. Michael, Eighteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA, 18, 785 (1981).
11. A. A. Westenberg and N. deHaas, *J. Chem. Phys.* 46, 490 (1967).
12. P. Andresen and A. C. Luntz, *J. Chem. Phys.* 72, 5842 (1980).
13. (a) M. Menzinger and R. Wolfgang, *Angew. Chem. (Int'l. Ed.)* 8, 438 (1969); (b) R. L. LeRoy, *J. Phys. Chem.* 73, 4338 (1969).
14. A. C. Luntz and P. Andresen, *J. Chem. Phys.* 72, 5851 (1980).
15. H. S. Johnston and C. Parr, *J. Am. Chem. Soc.* 85, 2544 (1963); H. S. Johnston, "Gas Phase Reaction Rate Theory," Ronald, New York, 1966.
16. J. V. Michael, D. G. Keil and R. B. Klemm - to be published.

Table I. Rate Data for the Reaction of $O(^3P)$ with Neopentane
from Flash Photolysis-Resonance Fluorescence Experiments

T/K	Neopentane/mTorr	O ₂ /Torr	P _T ^a /Torr	F. E./kJ	K ^b /s ⁻¹	k ₁ ^b x 10 ¹⁴ / cm ³ molec ⁻¹ s ⁻¹
<u>528</u>	---	3.00	100	57-60	62 ± 2	---
	44.3	3.03	100	17	207 ± 2	17.9 ± 0.5
	44.3	3.03	100	34	206 ± 10	17.8 ± 1.5
	44.3	3.03	100	73	218 ± 6	19.3 ± 1.0
	---	3.00	50	46	94 ± 4	---
	107.3	2.98	50	27	479 ± 18	19.6 ± 1.1
	107.3	2.98	50	60	469 ± 15	19.1 ± 1.0
	---	0.60	30	94-98	137 ± 4	---
	142.6	0.60	30	60	605 ± 21	17.9 ± 1.0
	142.6	0.60	30	98	613 ± 9	18.8 ± 0.5
	142.6	0.60	30	135	594 ± 11	17.5 ± 0.6

$$\langle k_1 \rangle^c = (18.4 \pm 1.6) \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$$

<u>498</u>	---	4.01	100	27-41	58 ± 2	---
	70.4	4.00	100	4	209 ± 6	11.1 ± 0.6
	70.4	4.00	100	7	215 ± 3	11.5 ± 0.4
	101.0	4.02	100	6	266 ± 7	10.6 ± 0.5
	101.0	4.02	100	11	283 ± 14	11.5 ± 0.8
	---	0.40	100	32-57	39 ± 2	---
	136.6	0.40	100	14	328 ± 14	10.9 ± 0.6
	136.6	0.40	100	36	349 ± 16	11.7 ± 0.7
	136.6	0.40	100	73	335 ± 5	11.2 ± 0.3
	---	6.01	100	32-36	82 ± 1	---
	214.6	5.97	100	32	541 ± 44	11.0 ± 1.1
	214.6	5.97	100	46	534 ± 36	10.9 ± 0.9
	---	2.01	100	49-60	52 ± 2	---
	475.3	2.00	100	63	926 ± 120	9.5 ± 1.3

$$\langle k_1 \rangle^c = (11.0 \pm 1.2) \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$$

Table I. (cont.)

<u>458</u>	---	3.00	50	38-41	77 ± 1	---
	107.3	2.98	50	8	200 ± 4	5.44 ± 0.22
	107.3	2.98	50	17	206 ± 6	5.70 ± 0.31
	107.3	2.98	50	22	209 ± 20	5.84 ± 0.93
	107.3	2.98	50	29	204 ± 10	5.61 ± 0.49
$\langle k_1 \rangle^c = (5.65 \pm 0.34) \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$						
<u>440</u>	---	4.01	100	27-32	67 ± 1	---
	101.0	4.02	100	5	166 ± 17	4.47 ± 0.81
	101.0	4.02	100	9	170 ± 20	4.65 ± 0.95
$\langle k_1 \rangle^c = (4.56 \pm 1.36) \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$						
<u>415</u>	---	4.01	100	23-27	77 ± 1	---
	70.4	4.00	100	5	124 ± 2	2.87 ± 0.18
	101.0	4.02	100	4	136 ± 8	2.51 ± 0.38
$\langle k_1 \rangle^c = (2.69 \pm 0.80) \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$						

^aDiluent gas was 80% Ar and 20% N₂.

^b"Diffusion" data are averages of 3 or more replicate runs. Errors for K are standard errors of linear least squares fits in most cases; however, a few runs were analyzed graphically. Errors in k_1 are propagated from standard errors in K's and concentrations.

^cAveraged at each temperature, the errors are estimated to be two standard errors (i. e., 95% confidence).

Table II: Rate Data for the Reaction of $O(^3P)$ with Neopentane from
Discharge Flow-Resonance Fluorescence Experiments^a

T/K	P _T /Torr	ν/cm s ⁻¹	Neopentane/10 ¹⁴ molecule cm ⁻³	k _c /s ⁻¹
922 ± 1 ^b	2.41 ± 0.01	3420 ± 7	0.28	94 ± 4
			0.82	241 ± 10
			1.24	358 ± 8
			1.81	542 ± 15
			2.46	680 ± 17
k ₁ = (2.74 ± 0.20) × 10 ⁻¹² cm ³ molec ⁻¹ s ⁻¹ Δk _w = 20 ± 31 s ⁻¹				
917 ± 0	2.18 ± 0.01	3396 ± 14	0.35	138 ± 2
			0.58	223 ± 3
			1.02	377 ± 9
			1.46	533 ± 10
			1.92	653 ± 12
			2.05	740 ± 18
	2.55	885 ± 20		
k ₁ = (3.38 ± 0.16) × 10 ⁻¹² cm ³ molec ⁻¹ s ⁻¹ Δk _w = 27 ± 25 s ⁻¹				
908 ± 0	1.56 ± 0.00	3028 ± 14	0.26	80 ± 1
			0.47	141 ± 4
			0.81	248 ± 2
			1.27	379 ± 17
			1.98	618 ± 9
			2.57	749 ± 20
k ₁ = (2.96 ± 0.16) × 10 ⁻¹² cm ³ molec ⁻¹ s ⁻¹ Δk _w = 6 ± 24 s ⁻¹				
869 ± 1 ^b	2.33 ± 0.01	3255 ± 20	0.29	75 ± 2
			0.92	228 ± 3
			1.31	330 ± 3
			1.79	456 ± 12
			1.89	468 ± 25
	2.48	616 ± 6		
k ₁ = (2.48 ± 0.06) × 10 ⁻¹² cm ³ molec ⁻¹ s ⁻¹ Δk _w = 3 ± 10 s ⁻¹				

Table II. (cont.)

813 $\pm$ 0 ^b	2.37 $\pm$ 0.01	3074 $\pm$ 14	0.49	65 $\pm$ 3
			1.36	220 $\pm$ 6
			2.01	312 $\pm$ 10
			2.69	419 $\pm$ 11
			3.45	514 $\pm$ 10
$k_1 = (1.52 \pm 0.11) \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ $\Delta k_w = 3 \pm 24 \text{ s}^{-1}$				
809 $\pm$ 0	2.55 $\pm$ 0.00	3216 $\pm$ 11	0.27	61 $\pm$ 2
			1.02	223 $\pm$ 4
			1.41	311 $\pm$ 5
			2.23	484 $\pm$ 10
			2.87	638 $\pm$ 15
			3.54	758 $\pm$ 14
$k_1 = (2.16 \pm 0.06) \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ $\Delta k_w = 4 \pm 15 \text{ s}^{-1}$				
773 $\pm$ 0	2.26 $\pm$ 0.01	2975 $\pm$ 45	0.68	111 $\pm$ 4
			1.20	200 $\pm$ 5
			2.02	309 $\pm$ 6
			2.74	424 $\pm$ 10
			3.40	531 $\pm$ 10
			4.32	632 $\pm$ 9
$k_1 = (1.45 \pm 0.08) \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ $\Delta k_w = 21 \pm 22 \text{ s}^{-1}$				
730 $\pm$ 0	1.52 $\pm$ 0.00	2633 $\pm$ 11	0.87	101 $\pm$ 2
			1.56	190 $\pm$ 3
			2.09	249 $\pm$ 2
			2.44	287 $\pm$ 2
			3.43	399 $\pm$ 5
			4.87	547 $\pm$ 7
$k_1 = (1.11 \pm 0.04) \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ $\Delta k_w = 14 \pm 12 \text{ s}^{-1}$				

Table II. (cont.)

690 $\pm$ 2	1.98 $\pm$ 0.01	2623 $\pm$ 27	1.07	70 $\pm$ 3
			2.38	151 $\pm$ 6
			2.38	156 $\pm$ 2
			3.06	216 $\pm$ 3
			4.03	270 $\pm$ 2
			4.95	333 $\pm$ 3
			6.19	443 $\pm$ 6
$k_1 = (7.20 \pm 0.44) \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ $\Delta k_w = -13 \pm 17 \text{ s}^{-1}$				
649 $\pm$ 1	2.09 $\pm$ 0.01	1331 $\pm$ 5	0.50	36 $\pm$ 2
			0.73	55 $\pm$ 2
			1.48	104 $\pm$ 2
			1.51	110 $\pm$ 1
			1.74	128 $\pm$ 1
			2.32	167 $\pm$ 2
$k_1 = (7.17 \pm 0.28) \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ $\Delta k_w = 1 \pm 4 \text{ s}^{-1}$				
621 $\pm$ 2	2.41 $\pm$ 0.00	1292 $\pm$ 4	0.79	33 $\pm$ 1
			1.60	65 $\pm$ 2
			2.53	100 $\pm$ 1
			3.28	133 $\pm$ 1
			3.65	149 $\pm$ 2
$k_1 = (4.05 \pm 0.15) \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ $\Delta k_w = 0 \pm 4 \text{ s}^{-1}$				
601 $\pm$ 1	1.97 $\pm$ 0.01	2390 $\pm$ 23	1.78	65 $\pm$ 2
			3.48	129 $\pm$ 2
			5.06	202 $\pm$ 3
			6.11	239 $\pm$ 5
			7.90	288 $\pm$ 4
			9.64	350 $\pm$ 2
$k_1 = (3.62 \pm 0.30) \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ $\Delta k_w = 8 \pm 18 \text{ s}^{-1}$				

Table II. (cont.)

600 $\pm$ 0	3.57 $\pm$ 0.01	1306 $\pm$ 6	1.22	56 $\pm$ 5
			2.86	127 $\pm$ 1
			4.17	176 $\pm$ 2
			6.17	254 $\pm$ 4
			7.16	279 $\pm$ 6
			8.95	316 $\pm$ 6
			9.54	371 $\pm$ 7

$$k_1 = (3.54 \pm 0.36) \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$$

$$\Delta k_w = 23 \pm 24 \text{ s}^{-1}$$

556 $\pm$ 0	2.03 $\pm$ 0.01	1163 $\pm$ 5	1.69	53 $\pm$ 2
			2.54	74 $\pm$ 3
			3.64	108 $\pm$ 1
			5.18	151 $\pm$ 3
			5.27	154 $\pm$ 2
			6.94	194 $\pm$ 2

$$k_1 = (2.74 \pm 0.12) \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$$

$$\Delta k_w = 7 \pm 6 \text{ s}^{-1}$$

556 $\pm$ 0	2.08 $\pm$ 0.00	1177 $\pm$ 5	1.67	46 $\pm$ 1
			3.99	110 $\pm$ 3
			5.22	138 $\pm$ 2
			5.57	145 $\pm$ 1
			6.78	169 $\pm$ 1

$$k_1 = (2.43 \pm 0.22) \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$$

$$\Delta k_w = 9 \pm 11 \text{ s}^{-1}$$

515 $\pm$ 0	2.07 $\pm$ 0.01	1085 $\pm$ 15	2.26	36 $\pm$ 1
			3.96	54 $\pm$ 1
			8.23	112 $\pm$ 4
			8.73	112 $\pm$ 3
			14.3	191 $\pm$ 5

$$k_1 = (1.29 \pm 0.08) \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$$

$$\Delta k_w = 4 \pm 7 \text{ s}^{-1}$$

Table II. (cont.)

471 ± 0	1.91 ± 0.01	1004 ± 12	2.83	28 ± 1
			6.16	57 ± 2
			8.47	79 ± 1
			11.3	93 ± 4
			14.4	113 ± 1
			17.1	139 ± 3

$$k_1 = (7.45 \pm 0.70) \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$$

$$\Delta k_w = 10 \pm 8 \text{ s}^{-1}$$

469 ± 0	1.88 ± 0.00	986 ± 12	3.21	27 ± 2
			6.54	55 ± 1
			8.85	73 ± 1
			11.3	82 ± 3
			14.0	103 ± 1
			17.2	124 ± 6

$$k_1 = (6.77 \pm 0.58) \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$$

$$\Delta k_w = 9 \pm 6 \text{ s}^{-1}$$

427 ± 2	1.64 ± 0.00	1749 ± 49	6.65	30 ± 1
			11.5	41 ± 1
			19.2	67 ± 3
			30.8	107 ± 6

$$k_1 = (3.26 \pm 0.32) \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$$

$$\Delta k_w = 6 \pm 6 \text{ s}^{-1}$$

^aStandard deviations in k_c are at the 1σ level, and in k_1 and Δk_w at the 2σ level.

^bON/OFF mode. (see text)

FIGURE CAPTIONS

Fig. 1. Values of the apparent rate constants, k_1^{app} , with the DF-RF apparatus for $\text{O}(^3\text{P}) + \text{neo-C}_5\text{H}_{12}$ as a function of $[\text{O}]_0$. $T = 470\text{K}$, $P_T = 1.90$ Torr, $v = 990 \text{ cm s}^{-1}$. The limiting low $[\text{O}]_0$ rate constant is $7.1 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The abscissa is logarithmic for clarity of display.

Fig. 2. Typical first order decay plots for relative $[\text{O}]$ as a function of d in the "ON/OFF" neo- C_5H_{12} experiments (DF-RF apparatus). $T = 869\text{K}$, $P_T = 2.33$ Torr, $v = 3255 \text{ cm s}^{-1}$. In units of $10^{14} \text{ molecules cm}^{-3}$, $[\text{neo-C}_5\text{H}_{12}]$ is: $\bullet - 0.29$; $\square - 0.92$; $\circ - 1.31$; $\blacktriangledown - 1.79$; $\nabla - 1.89$; and $\Delta - 2.48$. $k_1 = (2.48 \pm 0.06) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (see Fig. 3).

Fig. 3. Plots of corrected first-order decay constants, k_c , for $\text{O}(^3\text{P}) + \text{neo-C}_5\text{H}_{12}$ (DF-RF apparatus). $\Delta - T = 469 \text{ K}$, $P_T = 1.88$ Torr, $v = 986 \text{ cm s}^{-1}$; $\circ - T = 566\text{K}$, $P_T = 2.03$ Torr, $v = 1163 \text{ cm s}^{-1}$, O_2 - free; $\square - T = 690\text{K}$, $P_T = 1.98$ Torr, $v = 2623 \text{ cm s}^{-1}$; $\bullet - 869\text{K}$, $P_T = 2.33$ Torr, $v = 3255 \text{ cm s}^{-1}$, "ON/OFF" method. Slopes give the k_1 values in Table II.

Fig. 4. Comparison of present kinetic results with those of others in Arrhenius form. $\bullet$ - FP-RF, this work (Table I); $\circ$ - DF-RF, this work (Table II). Solid line with dashed extrapolation is the least squares fit to the combined results (Tables I and III). Δ - result of Wright.³ $\blacktriangle\blacktriangle$ - Arrhenius expression of Hexron and Huie.⁴