methyl cyclobutyl ketone decomposition is about 3 kcal/mole greater than the activation energy of the isopropenylcyclobutane decomposition is consistent with this reasoning.

There is no *a priori* reason why the same mechanism, *i.e.*, formation of a biradical, used to explain the decomposition of methyl cyclobutyl ketone and concurrent formation of 6-methyl-3,4-dihydro-2H-pyran (6-MDHP) must also explain the decomposition of 6-MDHP which occurs under very similar conditions of temperature and pressure. If the decomposition of 6-MDHP results in the formation of the above biradical structures, the formation of methyl cyclobutyl ketone should be possible. The study of the decomposition of 6-MDHP, however, detected no methyl cyclobutyl ketone formation.

The rate constants for 6-MDHP and 3,4-dihydro-2H-pyran[12] over the temperature range 330–370° show that the 6-MDHP decomposition proceeds approximately 45% faster. In order to determine the change in activation energy caused by methyl substitution, a value of $10^{14.542}$ for A was assigned to both reactions and corresponding values of E were calculated. At 360° the activation energy of the methyl derivative was 0.7 kcal/mole less than that of dihydropyran. Murphy, *et al.*,[13] studied the isomerization of vinyl allyl ether and isopropenyl allyl ether and found the methyl derivative to have a 1.3 kcal/mole lower energy.

A comparison of the decomposition of the substituted and unsubstituted dihydropyrans with the decomposition of cyclohexene[14] indicates the former reactions to be less complicated by free radicals. This is undoubtedly due to the fact that dihydropyrans decompose at about 350°, while temperatures near 500°, which greatly increase the probability of free radical formation, are necessary for the decomposition of cyclohexene.

Acknowledgment. The author wishes to express her indebtedness to the late Professor W. D. Walters who suggested this study and supervised its progress. She wishes to thank Mr. Carl Whiteman for the use of his least-squares program and General Railway Signal Co. for the use of their IBM computer.

---

[12] C. A. Wellington, *J. Chem. Soc.*, in press.

[13] F. W. Schuler and G. W. Murphy, *J. Am. Chem. Soc.*, **72**, 3155 (1950); L. Stein and G. W. Murphy, *ibid.*, **74**, 1041 (1952).

[14] W. Tsang, *J. Chem. Phys.*, **42**, 1805 (1965), and references therein.

Competitive Reactions of the Excited Oxygen Atoms, O(^{1}D)

G. Paraskevopoulos and R. J. Cvetanović

Contribution from the Division of Chemistry,
National Research Council of Canada, Ottawa, Canada. *Received May 1, 1969*

Abstract: Competitive interaction of O(^{1}D) atoms, formed by photolysis of N_2O at 2139 Å, with neopentane and a number of other gases has been studied at room temperature. Formation of the ground-state oxygen atoms, O(^{3}P), in these experiments was followed by measuring the characteristic products of their addition to butene-1. It was found that under the conditions employed SF_6 and He did not interact with O(^{1}D), H_2, CH_4, and neopentane reacted to form products but did not deactivate O(^{1}D), while N_2, Xe, CO, and CO_2 deactivated O(^{1}D) to O(^{3}P). The rates of these processes, relative to the rate of reaction of O(^{1}D) with neopentane, k_5/k_2, were determined from the decrease in the yields of neopentanol when another gas was added. The k_5/k_2 values obtained (given in parentheses) are: neopentane (1.000), SF_6 (0), He (0), H_2 (0.254), CH_4 (0.315), N_2 (0.039), Xe (0.128), CO (0.074), CO_2 (0.126). Where a comparison is possible, the trend is in good agreement with the previous results from this laboratory obtained in very different systems. Carbon monoxide does not show an exalted reactivity toward O(^{1}D) atoms and, moreover, does not, under the conditions employed, chemically react with them to form CO_2 but deactivates them to the ground state, O(^{3}P).

The chemical behavior of the electronically excited oxygen atoms, O(^{1}D), is of considerable interest, and several studies of the interaction of O(^{1}D) with various gases have been reported in recent years. There is, however still a great deal of controversial information about the relative rates of these interactions and uncertainty whether they result in a collisional deactivation of O(^{1}D) to O(^{3}P), a reaction to form products, or both. It is necessary, therefore, to obtain further experimental information on these processes using as many different experimental techniques and sources of O(^{1}D) as feasible.

In earlier work in this laboratory with propane[1] and isobutane,[2] it has been established that in general O(^{1}D) reacts with paraffins in the following two ways: (a) by insertion into the CH bonds to form vibrationally "hot" alcohols which decompose or are stabilized depending on the pressure and the number of vibrational degrees of freedom of the paraffin and (b) by abstraction of hydrogen from the paraffin to form OH and alkyl radicals. The number of final products arising from all possible interactions and the direct photolysis of the initial products depends on the type of paraffin (with primary, secondary, or tertiary hydrogens) and could be quite large.[2] In a more recent study of the interaction of O(^{1}D) with neopentane,[3] it has been found, as might have been expected in view of the sym-

---

[1] H. Yamazaki and R. J. Cvetanović, *J. Chem. Phys.*, **41**, 3703 (1964).

[2] G. Paraskevopoulos and R. J. Cvetanović, *ibid.*, **50**, 590 (1969).

[3] G. Paraskevopoulos and R. J. Cvetanović, submitted for publication.

metry of this paraffin, that only two main products are formed and that there are no side reactions. Thus, insertion, the predominant reaction, results in neopentanol, which is completely stabilized at quite low pressures; hydrogen abstraction results in one radical (neopentyl), which can only combine with itself to form 2,2,5,5-tetramethylhexane, but cannot disproportionate to form an olefin. The decrease in neopentanol yield then, in experiments in which another gas has been added to compete with neopentane for $O(^1D)$, gives a measure of the reactivity toward $O(^1D)$ of the added gas relative to that of neopentane. When a scavenger of $O(^3P)$ such as butene-1[4] is also added, the characteristic products of the reaction of $O(^3P)$ with butene-1 give a measure of the deactivation of $O(^1D)$ to $O(^3P)$ by the added gas. The present paper describes the results of such experiments with SF_6, He, H_2, CH_4, N_2, Xe, CO, and CO_2 as the added gas. The data provide information about the manner of interaction (deactivation or chemical reaction) of these gases with $O(^1D)$ and have been used to calculate the relative rates of these processes.

Experimental Section

Excited oxygen atoms, $O(^1D)$, were generated by photolysis of N_2O at 2138 Å using the light from two Phillips 93106 E zinc lamps. The photolysis cell with Suprasil quartz windows and the mercury-free vacuum system have been described previously.[2] The condensable reactants were frozen over into the reaction cell in the conventional manner. Noncondensable gases (He, N_2, CO, H_2, CH_4) were admitted at higher pressures from a flask of larger volume into the reaction cell already containing vaporized condensable reactants. Sufficient time was allowed for the reactants to mix thoroughly by diffusion and convection before the photolysis.

The mercury-containing analytical system and the analytical procedure used have been described before.[2] In experiments with the noncondensible gases, measurement of N_2 was not possible; the contents of the cell after the irradiation were frozen, and the noncondensibles were pumped off very slowly through three liquid nitrogen traps. When all the noncondensibles were completely removed, the condensibles were distilled into the mixing bulb and treated as described previously.[2] The analyses were made on a 300-ft 0.015-in. i.d. stainless steel capillary column coated with β,β'-thiodipropionitrile, operated at room temperature and equipped with a hydrogen flame ionization detector. Qualitative identification was based on the retention times and on seeding with authentic samples. Quantitative determinations were based on peak area measurements with toluene as an internal standard.

It is convenient to express all product yields relative to N_2, which is generated simultaneously with $O(^1D)$ and serves as an internal actinometer.[2] As mentioned above, it was not possible to collect and measure the small amounts of N_2 formed in the presence of the large excess of noncondensable gases that were used in most of the experiments. Nitrogen was therefore measured in every third experiment with SF_6 or CO_2 as the added gas and the yield of N_2 in the intervening experiments was estimated by interpolation. The ratios of the reactants (butene-1 : N_2O : neopentane : added gas), the current through the two zinc lamps (0.9 A), and the reaction time (1200 min) were kept the same in all the experiments. The yield of N_2 showed small fluctuations, but generally it decreased gradually with time from about 5 μmoles to about 2 μmoles in the course of 24 experiments of 1200 min each. This decrease was due to the aging of the lamps and perhaps to minute amounts of opaque deposit that is possibly formed on the cell windows.

The total error, analytical and due to the determination of N_2 by interpolation, is estimated to be about 10–15% but is in no case greater than 20%.

The materials used were: Phillips 66 Research Grade neopentane (stated purity 99.88%), Matheson nitrous oxide (stated purity 98.8%), Matheson sulfur hexafluoride (stated purity 98.0% minimum), Matheson Bone Dry carbon dioxide (stated purity 99.8% minimum), and Research Grade xenon. The neopentane was shaken in a bulb with concentrated sulfuric acid to remove any traces of olefin impurities and then passed through a column containing KOH pellets. All the reagents were subjected to three bulb-to-bulb distillations *in vacuo*, the last from a Dry Ice–acetone bath. They were further degassed at −196° before each experiment. The noncondensible reagents were Matheson Research Grade helium, Ultra Pure Grade hydrogen, Research Grade methane (stated purity 99.5%), CP Grade carbon monoxide (stated purity 99.5% minimum), and Prepurified nitrogen (stated purity 99.996%). They were used without further purification except for carbon monoxide which was passed through a Dry Ice–acetone trap filled with glass beads to remove any traces of iron carbonyl impurity.

Results

The reaction of $O(^1D)$ with neopentane has been found[3] to give mainly neopentanol and 2,2,5,5-tetramethylhexane together with very small amounts of pivalaldehyde and 2,2,4,4-tetramethylpentane. All the alcohol is stabilized at the pressures used in the present study. The experiments were made at 25 ± 2°. At the constant reaction time of 1200 min used, the conversion of neopentane was below 3%. The mixtures of the reactants used had the approximate composition: butene-1, 2 Torr; N_2O, 20 Torr; neopentane, 60 Torr; and the added gas, 620 Torr.

The yields of the products at neopentane/N_2O ratios of 15:1 and 3:1 with and without SF_6 are shown in Table I. The yields of neopentanol are within the experimental error the same in all three columns, indicating that in these experiments SF_6 does not interact in any way with $O(^1D)$, in agreement with previous work.[1,5–7] It is also clear that the alcohol yield is not affected by the 3:1 neopentane/N_2O ratio used in this work. Approximate calculations based on the rates measured in this work and on the data in the literature[5,6] show that at this ratio N_2 and O_2 are produced in a secondary attack of $O(^1D)$ on N_2O in amounts of less than 1% per $O(^1D)$. The small amount of O_2 will scavenge free radicals in the system, and indeed the yields of the free-radical products 2,2,5,5-tetramethylhexane and 2,2,4,4-tetramethylpentane decrease when a 3:1 ratio is used. This effect is not significant in the present work because hydrocarbon products are not measured.

Table I. Reaction of $O(^1D)$ Atoms with Neopentane[a]

Neopentane/N_2O	15:1	3:1	3:1
SF_6, Torr	None	None	619
Total pressure, Torr	830	780	698
Product Yields Relative to N_2 (*i.e.*, per $O(^1D)$)			
Neopentanol	0.654	0.640	0.630
Pivalaldehyde	0.011	0.027	0.024
2,2,5,5-Tetramethylhexane	0.247	0.159	nd[b]
2,2,4,4-Tetramethylpentane	0.020	0.013	nd[b]

[a] Effect of the neopentane/N_2O ratio and of the addition of SF_6 on the yields of the products. [b] nd = not determined.

The relative rate of reaction of $O(^3P)$ with neopentane and butene-1 is not known, but it is expected that with a ratio of neopentane/butene-1 of 30:1, any $O(^3P)$ formed will react almost exclusively with butene-1. The $O(^3P)$ reacts with paraffins by hydrogen abstraction with rates in the order: tertiary > secondary > primary. It reacts

---

[4] R. J. Cvetanović, *Advan. Photochem.*, **1**, 115 (1963).

[5] H. Yamazaki and R. J. Cvetanović, *J. Chem. Phys.*, **39**, 1902 (1963).

[6] K. F. Preston and R. J. Cvetanović, *ibid.*, **45**, 2888 (1966).

[7] H. Yamazaki and R. J. Cvetanović, *ibid.*, **40**, 582 (1964).

with butene-1 about 69 times faster than with isobutane[8] and about 128 times faster than with *n*-butane.[4] It can therefore be estimated conservatively that O(^{3}P) will react with butene-1 at least 300 times faster than with neopentane, which has only primary hydrogens. For our experimental conditions (neopentane/butene-1 ≈ 30:1), more than 90% of any O(^{3}P) formed in the system will react with butene-1 rather than with neopentane. Of the added gases, H_2, CH_4, and CO react very slowly with O(^{3}P). It was calculated[9] that for the added gas/butene-1 ratio of ~300:1 used all the O(^{3}P) formed will react with butene-1 rather than with H_2 or CH_4 and more than 80% of the O(^{3}P) will react with butene-1 rather than with CO. It is possible, therefore, to measure the extent of reaction of any added gas with O(^{1}D) from the decrease of the neopentanol yield when SF_6 is replaced by that gas, and the extent of deactivation of O(^{1}D) to O(^{3}P) from the yields of the products of the reaction of butene-1 with O(^{3}P), *i.e.*, 1,2-butene oxide, 1-butanal, and methyl ethyl ketone.[4] These last products will be referred to in this article as the "deactivation products."

The results are given in Table II. The upper part of the table shows the amounts of reactants used and the lower part, the yields of the products relative to N_2, *i.e.*, per O(^{1}D) atom formed. The yields of products with SF_6 as the added gas are given in the first column and are averages of four experiments. Since under the present experimental conditions SF_6 does not react with or deactivate O(^{1}D), these yields arise from the reaction of neopentane alone and are used for comparison with the yields when other gases are added. The data for the other added gases are given for each of the experiments to show the reproducibility.

In the case of the gases which deactivate O(^{1}D) to O(^{3}P), a rough estimate of the material balance of O(^{1}D) deactivated (Δn[O(^{1}D)]) and O(^{3}P) formed (Δn[O(^{3}P)]) is also given in Table II. It was calculated as follows. If Δn refers to the difference of the yields in the experiments with SF_6 and with a deactivating gas, $\Delta n[\mathrm{O}(^1\mathrm{D})] = 1.27\Delta n(\text{neopentanol}) + \Delta n(\text{pivalaldehyde})$. The factor 1.27 is related to the fraction of O(^{1}D) forming neopentanol and was calculated from the data of column 2 in Table I, *i.e.*, $1.27 = (0.64 + 0.159 + 0.013)/0.64$. Δn[O(^{3}P)] is the difference of the yields of the deactivation products (1,2-butene oxide, 1-butanal, and methyl ethyl ketone) in the experiments with the deactivating gas and with SF_6.

The bottom row of Table II gives the rate constants relative to neopentane for the reaction of the various added gases. These will be discussed in more detail in the following section.

It may be seen in the first column of Table II that very little deactivation occurs with neopentane alone (the total yield of deactivation products is about 2.5%). The yields of these products and of neopentanol are not affected when SF_6 is replaced by He. Addition of H_2 and CH_4 decreases significantly the yield of neopentanol but does not affect the total yield of deactivation products. On the other hand, addition of N_2, Xe, CO, and CO_2 results in a decrease in the yield of neopentanol and

Table II. Decrease in the Yields of O(^{1}D) Products (Neopentanol, Pivalaldehyde) and Increase in O(^{3}P) Products (1,2-Butene Oxide, 1-Butanal, Methyl Ethyl Ketone) in the Presence of Added Gases at 25 ± 2°

Additive	SF_6[a]	He	He	H_2	H_2	H_2	CH_4	CH_4	N_2	Xe	CO	CO	CO	CO_2	CO_2	CO_2	CO_2
Additive, Torr	615	616	627	625	608	614	616	620	622	612	644	627	629	604	632	632	637
Butene-1, Torr	2.24	2.20	2.18	2.24	2.19	2.18	2.29	2.23	2.21	2.20	2.20	2.27	2.17	2.17	2.19	2.20	2.19
N_2O, Torr	20.4	20.2	20.5	20.2	20.2	20.7	20.8	20.6	20.4	20.4	20.3	20.4	20.4	20.4	20.2	20.8	20.8
Neopentane, Torr	61.3	60.8	61.8	60.7	61.0	62.1	61.3	62.2	61.3	61.4	60.6	61.5	61.4	60.9	61.1	62.5	62.4
Total pressure, Torr	699	699	712	708	691	699	700	705	706	696	727	711	713	687	716	718	722
N_2, μmoles	3.7–5.0	4.37[b]	2.60[b]	4.11[b]	3.43[b]	3.36[b]	3.70[b]	2.92[b]	4.40[b]	3.83[b]	3.70[b]	4.14[b]	3.57[b]	3.96	3.63	3.17	2.10
							Rates of Product Formation Relative to $R_{N_2} = 1$										
Neopentanol	0.640	0.636	0.641	0.185	0.176	0.180	0.146	0.163	0.457	0.281	0.351	0.369	0.367	0.278	0.276	0.289	0.281
Pivalaldehyde	0.021	0.018	0.016	0.004	0.004	0.004	0.003	0.003	0.011	0.006	0.015	0.020	0.013	0.005	0.005	0.005	0.005
Propanol	0.016	0.017	0.013	0.010	0.009	0.007	0.013	0.010	0.013	0.014	0.017	0.019	0.014	0.013	0.013	0.013	0.013
1,2-Butene oxide	0.015	0.010	0.008	0.007	0.007	0.007	0.006	0.007	0.155	0.294	0.210	0.231	0.221	0.294	0.302	0.287	0.289
1-Butanal	0.011	0.009	0.009	0.015	0.013	0.014	0.020	0.025	0.088	0.166	0.130	0.146	0.134	0.161	0.169	0.193	0.198
Methyl ethyl ketone	tr[c]	tr	tr	0.004	0.004	0.003	tr	tr	0.006	0.011	0.021	0.025	0.021	0.009	0.010	0.009	0.010
Δn[O(^{1}D)]	...	~0	~0	0.595	0.606	0.601	0.645	0.624	0.242	0.471	0.373	0.345	0.355	0.476	0.478	0.462	0.472
Δn[O(^{3}P)]	...	~0	~0	~0	~0	~0	~0	~0	0.223	0.445	0.335	0.376	0.350	0.438	0.455	0.463	0.471
k_5/k_2	0	0	0	0.239	0.265	0.258	0.336	0.294	0.039	0.128	0.077	0.072	0.073	0.131	0.128	0.120	0.125

[a] Average of four experiments. [b] Calculated by interpolation as explained in the text. [c] tr = trace.

---

(8) R. J. Cvetanović and L. C. Doyle, unpublished results.

(9) The value for the rate constant for butene-1 is from ref 4 using the absolute value for O(^{3}P) + NO_2 of F. S. Klein and J. T. Herron, *J. Chem. Phys.*, **41**, 1285 (1964), and the values for H_2, CH_4, and CO are from K. Schofield, *Planetary Space Sci.*, **15**, 643 (1967).

a roughly equivalent increase in the yields of the deactivation products.

In all the experiments with added butene-1, minor amounts of propanal (1.5%) are formed and are most likely the product of O(^{1}D) attack on butene-1.[10]

Discussion

The following reaction scheme represents the main features[3] of the reaction of O(^{1}D), produced by photolysis of N_2O at 2139 Å, with neopentane (RH) in the presence of added gases (A).

$$N_2O + h\nu\ (2139\ \text{Å}) \longrightarrow N_2 + O(^1D) \quad (1)$$

$$\longrightarrow N_2 + O(^3P) \quad (1a)$$

$$RH + O(^1D) \longrightarrow ROH^* \quad (2a)$$

$$\longrightarrow R + OH \quad (2b)$$

$$\longrightarrow RH + O(^3P) \quad (2c)$$

$$ROH^* \longrightarrow \text{fragmentation} \quad (3)$$

$$ROH^* + M \longrightarrow ROH + M \quad (4)$$

$$A + O(^1D) \longrightarrow \text{products} \quad (5a)$$

$$\longrightarrow A + O(^3P) \quad (5b)$$

Reaction 1a is spin forbidden and is less likely than reaction 1, but it cannot be ruled out *a priori* because of the possibility of intersystem crossing to a repulsive triplet state. The present data show, as will be discussed below, that it may at best occur to a very small extent (<3%).

The major product of the reaction of O(^{1}D) with neopentane (RH) is neopentanol (ROH) which is initially formed with large vibrational excitation (ROH*). The lifetime of ROH* is sufficiently long that, at the pressures used in this work, it is completely stabilized in collisions with other molecules (M) present in the reaction mixture.[3] Reaction 3 therefore does not occur to any significant extent.

Collisional Deactivation and Chemical Reactions of O(^{1}D) with Paraffins and H_2. A question of interest is whether collisional deactivation of O(^{1}D) to O(^{3}P) occurs besides the insertion and abstraction when O(^{1}D) interacts with paraffins and hydrogen. From the data in Table II it is clear that neopentane does not deactivate O(^{1}D) to any significant extent; *i.e.*, reaction 2c is not important. With added SF_6 the total amount of the deactivation products is 2.5% of the O(^{1}D) atoms consumed. This places an upper limit on the fraction of O(^{3}P) atoms in the system, and thus of both reactions 1a and 2c together, at less than 3%. It would not be possible to say whether the small amount of O(^{3}P) present indicates a very minor occurrence of reaction 1a or 2c or both.

It may be argued that O(^{3}P) atoms formed in either of these two reactions (1a and 2c) may possess appreciable excess of translational energy and thus be preferentially scavenged by neopentane. However, Table II shows that substitution of SF_6 by helium, which is a good deactivator of translational excitation, does not alter the yields of the deactivation products, showing absence of translationally "hot" O(^{3}P) atoms. The same question was considered and similar conclusions drawn for the reaction of O(^{1}D) with isobutane.[2]

With SF_6 replaced by H_2 or CH_4, the total yields of the deactivation products remained unchanged[11] (~2.5%), indicating that deactivation of O(^{1}D) to O(^{3}P) by these gases is insignificant. On the other hand, the yield of neopentanol was decreased significantly, showing that these gases remove O(^{1}D) by chemical reaction. As with other paraffins,[1-3] it seems likely that this reaction involves insertion of O(^{1}D) into the H–H and CH bonds of hydrogen and methane to form "hot" H_2O and CH_3OH, and hydrogen abstraction to form H + OH and CH_3 + OH, respectively. However, because of the exothermicity of the reaction and the few degrees of freedom of the "hot" products, their lifetimes would be extremely short, and at the pressures used they would undergo complete fragmentation into H + OH and CH_3 + OH. To illustrate this point, it may be mentioned that the "hot" propanols resulting from the reaction of O(^{1}D) with propane[1] were only partially stabilized at pressures as high as 2500 Torr. It would not be possible, therefore, to assess the relative contributions of the two processes, or indeed to distinguish between them in the gas phase. In any case, H, CH_3, and partly OH, the last perhaps with some vibrational excitation,[12] probably interact with butene-1, and the resulting radicals are consumed in recombination and disproportionation reactions to form a variety of minor products. Small amounts (3.5%) of 1-butanol, formed in this manner, were observed in the experiments with hydrogen and methane. The slight increase in the yields of 1-butanal and methyl ethyl ketone over those of 1,2-butene oxide mentioned before[11] may be also attributed to reactions of this type.

De More[13] and De More and Raper[14] have investigated the reactions of O(^{1}D) with hydrogen and methane dissolved in liquid argon at 87°K. The present results and conclusions are in good agreement with those of De More and Raper except for methane, for which, besides the insertion and abstraction, they find that deactivation of O(^{1}D) to O(^{3}P) accounts for 30% of the total reaction, while no deactivation is observed in the present study. Although their work was conducted under very different experimental conditions (liquid phase and low temperature), we see no obvious reasons for this discrepancy.

Interaction of O(^{1}D) with N_2, Xe, CO, and CO_2. In contrast with hydrogen and methane, additions of N_2, Xe, CO, and CO_2 induce not only a decrease in the yield of neopentanol but also a corresponding increase in the yields of the deactivation products. Although the estimates of the material balance of O(^{1}D) and the O(^{3}P) formed by deactivation are approximate and may perhaps be in error by as much as 20%, the results in Table II clearly show that, within this error, all the O(^{1}D) atoms reacting with N_2, Xe, CO, and CO_2 appear as O(^{3}P) products, indicating that under conditions of these experiments, *i.e.*, in the gas phase at 25° and at pressures of up to 1 atm, deactivation of O(^{1}D)

---

(10) K. F. Preston and R. J. Cvetanović, *Ber. Bunsenges. Physik. Chem.*, **72**, 177 (1968).

(11) The total yield of the deactivation products remained unchanged with H_2 or CH_4, but, as may be seen in Table II, the yield of 1-butanal and in the case of H_2 also the yield of methyl ethyl ketone increased slightly relative to that of 1,2-butene oxide. It seems likely that this is due to reactions (disproportionation) of the radicals formed by addition of OH to butene-1.

(12) N. Basco and R. G. W. Norrish, *Proc. Roy. Soc.* (London), **A260**, 293 (1961).

(13) W. B. DeMore, *J. Chem. Phys.*, **47**, 2777 (1967).

(14) W. B. De More and O. F. Raper, *J. Chem. Phys.*, **46**, 2500 (1967).

Table III. Rate Constants at 25° for the Total Interaction[a] of $O(^1D)$ with Various Gases Relative to the Rate Constant for Reaction with Neopentane k_5/k_2

Reactant	k_5/k_2	Reactant	k_5/k_2
Neopentane	1.000	N_2	0.039
SF_6	0	Xe	0.128
He	0	CO	0.074
H_2	0.254	CO_2	0.126
CH_4	0.315		

[a] Chemical reaction plus collisional deactivation.

Table IV. Comparison of the Over-All Relative Rates of Reaction[a] of $O(^1D)$ from Different Sources[b]

Reactant	N_2O photolysis 2139 Å This work	NO_2 photolysis 2288 Å Ref 6	N_2O photolysis 1849 Å Ref 1,7	O_3 photolysis 2537 Å Ref 24[c]	O_2 photolysis 1470 Å Ref 17[d]	Flash photolysis of O_2 Vacuum uv Ref 25
CO_2	1.00	1.00	1.00	...	1.00	1.00
SF_6	0	0	0	...	...	...
He	0	...	0.02	...	...	...
H_2	2.0	...	...	2.0	1.0	...
CH_4	2.5	...	...	2.3	1.1	...
Propane	...	4.67	...	4.9	...	...
Isobutane	6.6[e]	...	...	...	...	...
Neopentane	7.9	...	...	...	...	...
N_2	0.31	0.24	0.26	...	0.24	...
Xe	1.0	0.78	0.82	...	...	...
CO	0.59	...	...	...	0.28	55.0

[a] Chemical reaction plus collisional deactivation. [b] All rate constants are expressed relative to that of CO_2 taken as unity. [c] Since no value for CO_2 is available in this case, H_2 is taken as 2.0 in order to compare the other values with those in present work. [d] Three types of determination were made in ref 17; when this resulted in more than one value for the relative rate constant, the average value is quoted here. [e] Taken from ref 2.

to $O(^3P)$ is the only process that takes place. This conclusion is in good agreement with previous work in this laboratory[1,5–7] with N_2, Xe, and CO_2, that of De More and Raper[15,16] with N_2 and CO, and the more recent work of Young, *et al.*,[17] with N_2, CO_2, H_2, and CH_4.

In the case of CO there is disagreement in the literature as to whether it combines chemically with $O(^1D)$ to form an excited CO_2 which is eventually stabilized or if it merely deactivates $O(^1D)$ to $O(^3P)$. Thus, formation of long-lived excited CO_2 molecules which become stabilized by collisions has been postulated by Clerc and Barat,[18,19] who generated $O(^1D)$ atoms by vacuum uv flash photolysis of CO_2, and by Young, *et al.*,[17] who produced $O(^1D)$ by photolysis of 7–25 Torr of O_2 at 1470 Å. On the other hand, the work of Raper and De More[16] and the present results show that the electronic deactivation of $O(^1D)$ to $O(^3P)$, although spin forbidden, is the main mode of interaction. Raper and De More[16] produced $O(^1D)$ by photolyzing dilute solutions of O_3 in liquid CO at 77°K. The association complex formed between $O(^1D)$ and CO may be either the ground singlet of $CO_2(^1\Sigma_g^+)$ with about 172 kcal/mole of vibrational excitation energy or the excited CO_2 in the bent $^1B_2$ state with about 41 kcal/mole of vibrational excitation.[20] In general, the "complex" may (a) redissociate to the original reactants, (b) lose sufficient excitation energy in collisions or by radiation and be stabilized to CO_2, and (c) predissociate to CO + $O(^3P)$. Raper and De More[16] found in their work in the liquid phase that the deactivation of $O(^1D)$ to $O(^3P)$ was the predominant reaction and estimated that predissociation was about 15 times faster than the collisional stabilization to CO_2. In the gas phase, then, predominant predissociation would be expected, in agreement with the present results. The predissociation is a spin-forbidden process but may be expected to occur as a result of the crossing of the $^1\Sigma_g^+$ or $^1B_2$ states by the repulsive CO + $O(^3P)$ surface (there is apparently no bound triplet state of CO_2,[20] and the repulsive CO + $O(^3P)$ surface crosses the $^1\Sigma_g^+$ surface at about 127 kcal/mole).

In the reaction of $O(^1D)$ with CO_2, an intermediate CO_3^* complex has been postulated,[21] and recently evidence for its existence in solid matrices has been presented.[22,23] While it is most likely that a CO_3^* complex is indeed initially formed, it is evident that under conditions of the present experiments this intermediate decomposes to CO_2 and $O(^3P)$, and all the $O(^1D)$ atoms reacting with CO_2 appear as products of $O(^3P)$. It should be noted that the ratios of the deactivation products for CO_2 are, within the experimental error, the same as those for N_2, Xe, and CO, indicating that these products arise in this case also from the reaction of butene-1 with $O(^3P)$ and not with CO_3 (or CO_3^*).

Relative Rate Constants. At the pressures used in the present experiments the neopentanol formed is stabilized. For the reactions 1, 2, and 5, therefore, with the usual steady-state assumption, the following expression is obtained

$$\frac{k_5}{k_2} = \left(\frac{R^0}{R} - 1\right)\frac{[\mathrm{RH}]}{[\mathrm{A}]} \qquad (6)$$

R^0 is the rate of production of neopentanol when neopentane alone reacts with $O(^1D)$, *i.e.*, when SF_6, which does not interact with $O(^1D)$, is added; R is the rate of production of neopentanol when a gas [A] is added;

---

(15) W. B. De More and O. F. Raper, *J. Chem. Phys.*, **37**, 2048 (1962).
(16) O. F. Raper and W. B. De More, *ibid.*, **40**, 1053 (1964).
(17) R. A. Young, G. Black, and T. G. Slanger, *ibid.*, **49**, 4758 (1968).
(18) M. Clerc and F. Barat, *J. Chim. Phys.*, **63**, 1525 (1966).
(19) M. Clerc and F. Barat, *J. Chem. Phys.*, **46**, 107 (1967).
(20) G. Herzberg, "Electronic Spectra of Polyatomic Molecules," D. Van Nostrand Co., Princeton, N. J., 1966, pp 598, 431.
(21) D. Katakis and H. Taube, *J. Chem. Phys.*, **36**, 416 (1962).
(22) N. G. Moll, D. R. Clutter, and W. E. Thompson, *ibid.*, **45**, 4469 (1966).
(23) E. Weissberger, W. H. Breckenridge, and H. Taube, *ibid.*, **47**, 1764 (1967).

and [RH] stands for neopentane. The ratio R^0/R is the ratio of the relative yields of neopentanol in Table II.

The individual values of the relative rates k_5/k_2 obtained from eq 6 are given in the last row of Table II, and the average values are listed in Table III. In Table IV the relative rates from this work are compared with those found in other studies. In Table IV all the rates are expressed relative to that of CO_2 which provides a common basis.

The values obtained in this work agree well with those of other studies, determined in different systems and with $O(^1D)$ from different sources. The values for N_2 and Xe, obtained from single experiments, are evidently in line with those from previous work,[1,6,7] but the latter are based on more detailed determinations and are therefore more reliable quantitatively. SF_6 and He are found to be nonreactive as was observed before. The values for H_2, CH_4, and CO agree within a factor of 2 with those of Young, *et al.*[17] This agreement is perhaps as good as may be expected in view of the entirely different experimental techniques and the errors involved in both. The ratio k_{CH_4}/k_{H_2} = 1.24 estimated from the present results agrees well with the ratio of 1.15 found by De More.[24]

On the other hand, there is a very large discrepancy of two orders of magnitude between the somewhat similar values for CO obtained in the present work and by Young, *et al.*,[17] and that obtained by Clerc and Reiffsteck.[25] These values are 0.59, 0.28, and 55, respectively, and the difference is much larger than the experimental error in any of these studies. As already pointed out, both Young, *et al.*,[17] and Clerc and Reiffsteck produced $O(^1D)$ from O_2 by vacuum uv photolysis and flash photolysis, respectively, and both found $O(^1D)$ to react with CO to form CO_2, as opposed to deactivation to $O(^3P)$ observed in the present work. The reasons for these discrepancies are not known.

---

(24) W. B. De More, *J. Phys. Chem.*, 73, 391 (1969).

(25) M. Clerc and A. Reiffsteck, *J. Chem. Phys.*, **48**, 2799 (1968).

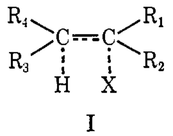
Gas-Phase Eliminations. XI.[1] The Pyrolysis of α-Chloro-*o*-xylene

A. G. Loudon, Allan Maccoll, and S. K. Wong

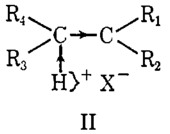
Contribution from the Williams Ramsay and Ralph Forster Laboratories, University College, London, W.C.1, England. *Received May 19, 1969*

Abstract: The kinetics of the pyrolysis of α-chloro-*o*-xylene to yield benzocyclobutene and hydrogen chloride in the temperature range 395–423° is reported. The reaction is first order, homogeneous, and unimolecular, the rate constants being expressed as $\log k_1 = 11.47 - (46{,}950/2.303RT)$ with k_1 in sec^{-1}. The facts are consistent with the decomposition occurring through a six-centered transition state.

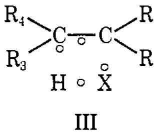
The pyrolysis of alkyl halides has been extensively studied in many laboratories. Evidence has been presented for the polar character of the reaction.[2] On the basis of substituent effects, at or near the reaction center, the originally proposed homolytic four-centered transition state I has been replaced by the ion pair II or semi-ion pair transition state III.



I

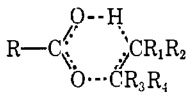


II

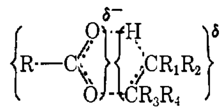


III

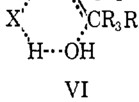
On the other hand, there is general agreement that the pyrolysis of esters proceeds through a six-centered transition state IV, as suggested by Hurd and Blunck.[3] However, in this case too, a degree of polar character, as represented by the transition state V, has been suggested to explain the observed substituent effects.[4] It has also been suggested that Cope[5a] and Claisen[5b] rearrangements proceed through a six-centered transition state.



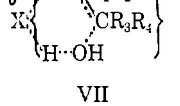
IV



V



VI



VII

The mechanism of the catalysis of the dehydration of alcohols by hydrogen halides has been investigated at length by Stimson and coworkers.[6] The transition state in this case can be represented by VI or VII. A similar type of transition state was postulated by Ross and the author,[7] to explain the hydrogen bromide catalysis of the

---

(1) Part X: M. Dakubu, and A. Maccoll, *J. Chem. Soc., B*, 1248 (1969).

(2) A. Maccoll and P. J. Thomas, *Progr. Reaction Kinetics*, **4**, 136 (1967).

(3) C. D. Hurd and F. H. Blunck, *J. Amer. Chem Soc.*, **60**, 2419 (1938).

(4) E. V. Emovon and A. Maccoll, *J. Chem. Soc.*, 227 (1964).

(5) (a) H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 103 (1969); (b) F. W. Schuler and G. W. Murphy, *J. Amer. Chem. Soc.*, **72**, 3155 (1950).

(6) J. T. D. Cross and V. R. Stimson, *Aust. J. Chem.*, **19**, 401 (1966).

(7) A. Maccoll and R. A. Ross, *J. Amer. Chem. Soc.*, **87**, 4997 (1965).