$$Cu_oA_2 + CCl_4 \rightleftharpoons Cu_oA_2 \cdot CCl_4 \qquad (8)$$

$$Cu_oA_2 \cdot CCl_4 \longrightarrow Cu(A_2)Cl + \cdot CCl_3 \qquad (9)$$

where Cu_o, Cu_oA, and Cu_oA_2 have the meaning introduced earlier, and $Cu_oA_2 \cdot CCl_4$ denotes a charge-transfer complex formed between adsorbed amine and CCl_4 at an oxidized site.

Reaction 9 is taken to be the rate-determining step, $Cu(A)_2Cl$ being written as the composition of the red layer. This layer dissolves rapidly and its cuprous ions are oxidized rapidly to cupric ions in solution by the oxygen and by the charge-transfer complex.[1] The other reaction products are accounted for by reactions[1] involving the trichloromethyl radicals formed in reaction 9.

This mechanism yields the rate expression

$$-\frac{dCu}{dt} = \frac{d[Cu^{2+}]}{dt} = \frac{k_9K_6K_7K_8fS[A]^2[CCl_4]}{1 + K_6[A] + K_6K_7[A]^2} \qquad (10)$$

where S is the surface area of the copper, f is the fraction of the area covered by oxidized sites, k_9 is the velocity constant of the rate-determining step, and K_6, K_7, and K_8 are the equilibrium constants of reactions 6, 7, and 8, respectively. If f is taken as constant when the oxygen pressure is constant, and since the CCl_4 is present in large excess, this rate expression becomes the same as that observed (eq 1).

The same result is obtained for the conditions of our experiments if the mechanism is altered to replace reactions 7 and 8 by a single process in which a preformed charge-transfer complex attaches to an oxidized site

$$Cu_oA + A \cdot CCl_4 \rightleftharpoons Cu_oA_2 \cdot CCl_4 \qquad (11)$$

but we prefer the use of reactions 7 and 8 because of the earlier extensive work,[11] which proved the rapid adsorption of two molecules of amine to each oxidized site, and also because of the low concentration of the charge-transfer complexes in the solution.[1]

Preliminary experiments showed that the protonated amine is nearly as effective as amine in dissolving copper in our systems. This may be accounted for, as in the case of the aqueous systems,[11] by transfer of the proton to oxygen attached to the activated site. In the two runs in which the amine hydrochloride was added to the system instead of amine, induction periods of 2 and 7 min occurred and the red layer did not appear until the induction periods ended and the copper started to dissolve.

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Rates of Ozone–Paraffin Reactions in Carbon Tetrachloride Solution[1]

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Abstract: The second-order rate constants of ozonation in carbon tetrachloride solution at 25° have been determined for nine paraffins: isobutane, *n*-pentane, isopentane, neopentane, 3-methylpentane, 2,3-dimethylbutane, *n*-octane, cyclopentane, and cyclohexane. Different types of CH bonds in the paraffin molecules show large differences in reactivity, with primary < secondary < tertiary. Rate constants have been also determined for the following three alcohols: *t*-butyl alcohol, *n*-butyl alcohol, and cyclopentanol, and are found to increase rapidly in that order.

Reactions of ozone with unsaturated hydrocarbons have been investigated very extensively.[3] Much less work has been done on the corresponding reactions with saturated hydrocarbons and, in particular, relatively few determinations of the absolute values of second-order rate constants for ozone–paraffin reactions have been made. Schubert and Pease[4] have determined the second-order rate constants in the gas phase for methane, propane, *n*-butane, and isobutane and found that they depend on the strength of the CH bonds in the paraffins. This was shown by a 14-fold increase in the rate constant at 25° and a decrease in activation energy from 14.9 to 10.3 kcal/mol in going from methane, which has only primary H atoms, to isobutane, which has a tertiary H atom. On the other hand, in subsequent extensions of this work, Schubert and coworkers[5,6] have found no difference in the activation energies of methane, ethane, and propane and, surprisingly, a somewhat *greater* reactivity of the primary H atoms in ethane than of the less strongly bound secondary H atoms in propane. Hamilton, Ribner, and

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[1] Issued as NRC No. 11330.

[2] National Research Council Postdoctorate Fellow.

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[4] C. C. Schubert and R. N. Pease, *J. Chem. Phys.*, **24**, 919 (1956); *J. Amer. Chem. Soc.*, **78**, 2044 (1956).

[5] F. J. Dillemouth, D. R. Skidmore, and C. C. Schubert, *J. Phys. Chem.*, **64**, 1496 (1960).

[6] R. J. Morrissey and C. C. Schubert, *Combust. Flame*, **7**, 263 (1963).

Hellman[7] have recently determined, from the ratios of the four C_5 alcohols formed in the ozonation of liquid isopentane at 0°, the following relative reactivities per hydrogen atom: primary, 1; secondary, 13; tertiary, 110.

The present experimental work has been concerned with the determination of the second-order rate constants for the ozonation of several representative paraffins in carbon tetrachloride solutions. It is an extension of our earlier studies of the rates of ozonation of olefins[8] and chlorinated and conjugated olefins,[9] prompted in part by the potential importance of these reactions for the understanding of the chemical processes which occur in polluted atmosphere.

Experimental Section

The change in ozone concentration as a function of time was measured spectrophotometrically with a Beckmann DU spectrophotometer equipped with an energy recording adapter.[8,9] Typical reaction half-lives were of the order of 5–10 min and the rate measurements could be done in a conventional way.[10] An aliquot of a paraffin–carbon tetrachloride solution of known concentration was pipeted into a 100-ml volumetric flask. The contents of the flask were diluted up to about 95 ml and 2–5 ml of carbon tetrachloride containing ozone was then added; the resulting reactant solution was made up with carbon tetrachloride to 100.0 ml and well mixed. A 10-cm path length spectrophotometric cell served as a reaction vessel, and the absorbance of the solution was determined as a function of time. The reference cell contained the paraffin dissolved in carbon tetrachloride at the same concentration as in the reaction cell. All experiments were done at room temperature, 25 ± 1°. Baker–Adamson Research Grade CCl_4 was used as the solvent after pretreatment with ozone.[8–10]

The isopentane, isobutane, 3-methylpentane, diisopropyl, *n*-octane, and neopentane used in the present experiments were all Phillips Research Grade hydrocarbons. Anachemia Reagent Grade *n*-pentane, Matheson Coleman and Bell cyclopentane, and the chromatographic grade cyclohexane were also used. Any traces of olefin impurities were removed by shaking the paraffin with concentrated sulfuric acid several times in a separatory funnel. The paraffin was subsequently washed with 0.1 *N* NaOH and with water and was then dried with anhydrous sodium sulfate.

Results

Rates of ozone decay were measured under conditions of excess paraffin so that the pseudo-first-order rate constants for ozone depletion could be determined. A simple bimolecular reaction was assumed for the first step of the reaction and it was also assumed that ozone was not consumed to a significant extent by any secondary reactions with products. Values for k_1 were

$$\mathrm{RH} + \mathrm{O} \xrightarrow{k_1} \text{products}$$

calculated from the observed value of k_1', where

$$k_1' = 0.693/t_{1/2}$$

$t_{1/2}$ is the half-life of the ozone, and

$$k_1 = k_1'/(\text{initial paraffin concentration})$$

In all experiments $[\text{paraffin}]_{\text{initial}} \gg [O_3]_{\text{initial}}$ so that the paraffin concentration was essentially constant throughout the reaction. The ozone concentration was monitored at 2900 Å where $\epsilon_{O_3} = 7.89 \times 10^5$ cc mol^{-1} cm^{-1} Representative first-order plots are shown in Figures 1 and 2 for *n*-octane and 3-methylpentane. Table I shows the values of k_1 obtained for a number of ozone–paraffin reactions and, for comparison, several literature values for related compounds.

Table I. Second-Order Rate Constants for Paraffin–Ozone Reactions in CCl_4 Solution at 25 ± 1°

Paraffin	k_1, cc/mol^{-1} sec^{-1}	k_1, rel
2,3-Dimethylbutane	200	1.00
3-Methylpentane	100	0.50
Isobutane	87	0.44
Isopentane	70	0.35
Cyclopentane	26	0.13
Cyclohexane	10.5	0.053
n-Octane	14	0.070
n-Pentane	6.5	0.033
Neopentane	0.038	0.00019
Lit. Values for Several Related Compounds		
Benzene[10]	28	0.14
$CCl_2{=}CCl_2$[9]	1000	5
1-Pentene[8]	8×10^7	4×10^5
2,3-Dimethyl-2-butene[8]	2×10^8	1×10^6

Some variation of k_1 with concentration was detected. In all cases, k_1 showed an increase at smaller initial paraffin concentration, although this trend was more pronounced with normal paraffins than those containing tertiary CH bonds, which were considerably more reactive. Figure 3 shows the variations in k_1 for *n*-pentane and *n*-octane, and Figure 4 for isopentane and 3-methylpentane. The exact reason for the increase in the rates at smaller paraffin concentrations is not known, although it is probably caused by consumption of ozone in reactions with impurities or in side reactions. The k_1 values in Table I are the plateau values at high initial paraffin concentrations which should be free from this complication.

The effect of small amounts of olefin impurities on the measured second-order rate constants was determined by adding a small quantity (0.05%) of 1-hexene to 3-methylpentane dissolved in CCl_4. After an initial very rapid reaction of the added 1-hexene, the first-order decay curve is affected seriously only after the reaction is about 90% complete with respect to ozone. At this time, the decrease in absorbance with time flattens out. To test whether this absorbance is actually due to O_3, an amount of 1-hexene sufficient to react with all residual ozone present was added to the reactant solution well after the reaction was 90% complete. The absorbance did not rapidly decrease to zero. Therefore, ozone was not the principal absorbing species after 90% reaction time. Perhaps the absorbance observed in the presence of the small amount of 1-hexene impurity could be due to peroxidic or carbonyl products from the ozone–1-hexene reaction.

Table II shows the results of stoichiometric measurements on some ozone–paraffin reactions. In these experiments ozone containing oxygen was bubbled through the solution of the paraffin in carbon tetrachloride and the results have been corrected for any evaporation of paraffin. Correction for evaporation was large for isopentane, since sometimes as much as 25% of the isopentane evaporated during the reaction. Evaporation could be one reason for the large amount of scatter in the results. Only a small correction for evaporation was necessary with 3-methylpentane.

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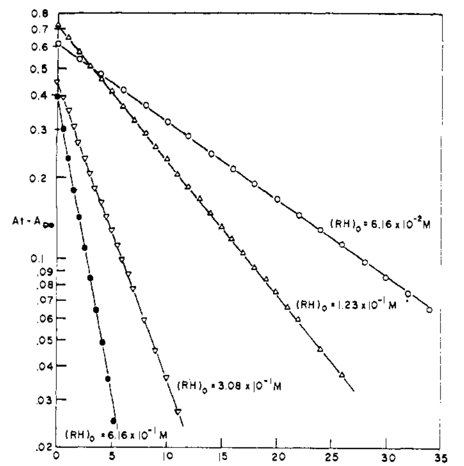

Figure 1. First-order decay of ozone in the presence of various concentrations of *n*-octane.

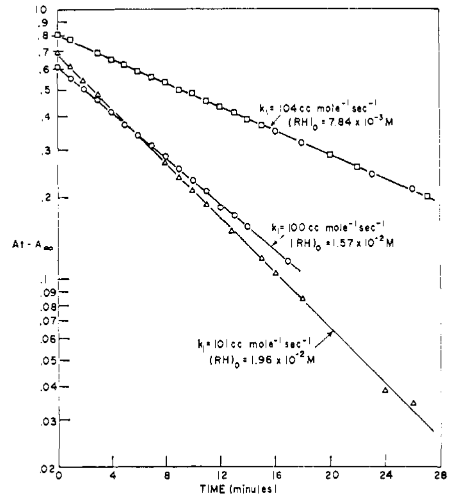

Figure 2. First-order decay of ozone in the presence of various concentrations of 3-methylpentane.

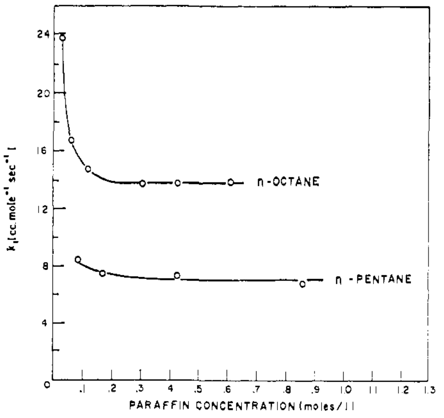

Figure 3. Variation of the second-order rate constants with the concentration of *n*-octane and *n*-pentane.

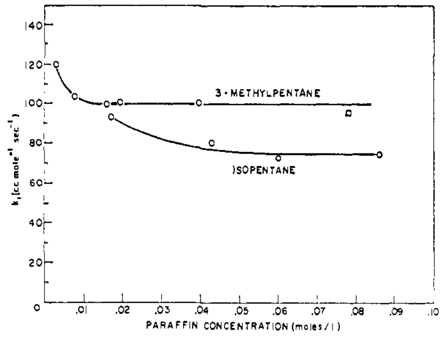

Figure 4. Variation of the second-order rate constants with the concentration of isopentane and 3-methylpentane.

The results in Table II suggest that chain decomposition processes leading to large consumption of paraffin substrate or ozone appear to be unimportant under present experimental conditions. Values of the ratio (mmol paraffin consumed)/(mmol O_3 absorbed) smaller than one could be the result of reaction of O_3 with product alcohols in these high conversion experiments in which about 20–25% of the paraffins reacted. It is known that alcohols are readily oxidized by ozone. Stoichiometry of approximately 1 : 1 is in agreement with findings in gas-phase ozone–paraffin experiments.[4–6] Simple 1 : 1 stoichiometry has been assumed for the evaluation of the rate constants.

Table II. Stoichiometry of Some Ozone–Paraffin Reactions

	O_3 added, mmol	O_3 absorbed, mmol	paraffin reacted, mmol	mmol of paraffin reacted/ mmol of O_3 abs
Isopentane	6.32	2.20	1.98	0.90
	5.79	1.46	1.87	1.28
	5.83	2.16	1.92	0.89
3-Methylpentane	6.73	2.98	2.03	0.68
	1.42	0.29	0.20	0.69

The decay rate of ozone was also measured in the presence of cyclopentanol, *n*-butyl alcohol, and *t*-butyl alcohol (Table III). The cyclopentanol was Matheson Coleman and Bell chromatographic quality and was used without further purification. Neither the *n*-butyl alcohol nor the *t*-butyl alcohol showed any impurities when analyzed on 300-ft squalane or β,β′-thiodipropionitrile capillary columns.

Table III. Second-Order Rate Constants for Ozone–Alcohol Reactions in CCl_4 Solution at 25°

Alcohol	k_1, cc mol⁻¹ sec⁻¹	k_1, rel
Cyclopentanol	1350	27
n-Butyl alcohol	390	8
t-Butyl alcohol	50	1

Alcohols are reactive enough to interfere under some conditions in the determination of rates of O_3–paraffin reactions. For instance, the calculated second-order rate constant for *n*-pentane is about 6.5 cc mol^{-1} sec^{-1}, whereas the rate for a secondary alcohol is about 1400 cc mol^{-1} sec^{-1}. If the reaction were allowed to go to 0.5% of the *n*-pentane present initially, then the rate of ozone consumption due to reaction with the alcohol would be equal to the reaction rate with the paraffin itself. Of course in this calculation it is assumed that the yield of alcohol from the paraffin is

100%. The lowest concentration of *n*-pentane used was 8.6×10^{-2} *M* with $[O_3]_{\text{initial}} = 9 \times 10^{-5}$ *M*. At 100% reaction of ozone, and assuming that the alcohol is produced in 100% yield

$$\frac{\text{rate of attack on alcohol}}{\text{rate of attack on paraffin}} = 0.20$$

Such an effect could contribute to the observed increase in rate at low concentration. But the rate plots at low paraffin concentrations do not show a significant increase of k_1 even at high ozone conversion which suggests that secondary reactions with the product alcohols is not too important. However, it should be remembered that a small curvature on a log plot is not easy to notice. A similar treatment for 3-methylpentane shows that at 100% reaction at low initial paraffin concentration

$$\frac{\text{rate of attack on } t\text{-butyl alcohol}}{\text{rate of attack on 3-methylbutane}} = 0.014$$

This contribution is too small to account for the increase in k_1 at low concentration.

The most significant role of secondary attack on alcohol products would be with neopentane, for which

$$\frac{\text{rate of attack on neopentyl alcohol}}{\text{rate of attack on neopentane}} = 0.83$$

at 100% reaction. Clearly, the determined rate for neopentane is an upper limit, at best.

Only a brief attempt at product analysis was made. In particular, an attempt was made to verify approximately the large difference in reactivity between neopentane and isopentane shown in Table I by direct analysis of the products formed in a competitive experiment. A solution of neopentane in isopentane such that [neopentane] = [isopentane] was ozonized at 0° and the products were analyzed on a 300-ft β,β'-thiodipropionitrile capillary column. The major product was *t*-amyl alcohol. No neopentyl alcohol could be detected after ozonation for about 45 min. This suggests that the reactivity of the tertiary CH in isopentane to that of the primary CH in neopentane is $\geqslant 14000$, which is consistent with the rate constants in Table I. It should be noted that the products were not reduced with $LiAlH_4$ before analysis, as was done by Hamilton, *et al.*[7] A number of other minor peaks were eluted but not identified.

Discussion

It is evident from Tables I and III that in CCl_4 solution at 25° paraffins and alcohols react with ozone many orders of magnitude less rapidly than olefins. Their reactivities are approximately comparable to that of benzene[10] and are strongly structure sensitive.

The rate constants for paraffins in Table I are roughly similar to the gas-phase values.[4-6] The value for *n*-pentane (6.5 cc mol^{-1} sec^{-1}) is practically the same as obtained by Schubert and Pease for *n*-butane (5.9 cc mol^{-1} sec^{-1}), but the value for isobutane is larger than the gas-phase value[4] by a factor of 7. For the lighter paraffins (CH_4, C_2H_6, C_3H_8) studied in the gas phase,[4-6] a determination of rate constants by present technique is not feasible.

Table I clearly shows a strong dependence of the rate constants on the type of CH bonds in paraffins. The order of reactivity is tertiary > secondary > primary, which is the same as found by Hamilton, *et al.*,[7] although the differences in reactivity are larger. The ratio of reactivities per H atom found by these authors is tertiary:secondary:primary = 1:0.077:0.0091, while the present data would indicate (with some variation) 1:0.01:0.000033. A quantitative comparison of these two results, however, is not too straightforward.

It is possible, first, that the relatively slow reactions of ozone with paraffins are subject to a large solvent effect and that the larger differences in reactivity observed in the present work may be due to an increased discrimination of ozone attack on paraffins in CCl_4 solution. Another possibility is that neopentane may be exceptional and that it does not provide a true measure of reactivity of primary H atoms in general. The data in Table I show some variation and indicate that the reactivity of a type of H atoms may depend also on its environment in the molecule. On the other hand, if even small amounts of some rapidly reacting (and therefore not too discriminating) free radicals are formed, such as alkoxy[4] or OH,[11] they could have a large effect on an experiment of the kind carried out by Hamilton, *et al.*, since they would abstract more indiscriminately primary H atoms and lead indirectly to the formation of the corresponding alcohols. Such a contribution, even if relatively minor, could affect seriously the calculated ratios of the initial attack on ozone at various positions in the molecule since ozone itself reacts very slowly with primary H atoms. Before these various possibilities can be resolved, a more extensive and more detailed investigation of the initial products of ozonation of different paraffins will be necessary.[12] Such information would also help to establish the detailed mechanism of ozone attack on paraffins.[4,7,11]

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(11) V. J. Dardin, Jr., and L. F. Albright, *Ind. Eng. Chem., Process Des. Develop.*, 4, 61 (1965).

(12) The authors are grateful to a referee of this paper for suggesting the following additional potential reasons for the difference in the relative H-bond reactivities observed in present work and by Hamilton, *et al.*[7] (1) Inasmuch as free radicals may be involved in the reaction, the presence of excess O_2 may perhaps have an effect on the results. (2) Any products formed during the pretreatment of the CCl_4 solvent by ozone[9] might have different effects on the various hydrocarbon substrates used. (3) The results may be affected by the slight difference in temperature in the two studies. The possibility that these effects may be of some significance merits further investigation, although there are no indications at the moment that they are important.