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Removal Rate Constants for Singlet Methylene with Oxygen-Containing Organic Species

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The technique of laser flash photolysis/laser absorption has been used to obtain absolute removal rate constants for singlet methylene, $^1CH_2$ ($\tilde{a}\ ^1A_1$), with various oxygen-containing organic species. Removal rate constants for some 27 alcohols, ethers, ketones, aldehydes, carboxylic acids, and esters are reported for the first time. The removal rate constants for H_2O and CH_3OH have been remeasured and found to be in excellent agreement with values determined by other researchers. Improved removal rate constants for C_2H_5OH, n-C_3H_7OH, CH_3OCH_3, CH_3CHO, CH_3COCH_3, CH_3COOH, $HCOOCH_3$, and $CH_3OCOOCH_3$ are also presented. In all cases the removal rate constants are large, indicating that reaction is the dominant process leading to loss of $^1CH_2$. Comparisons are drawn between the reactivities of the various functional groups and between them and their hydrocarbon analogues. Because of the large data base provided by these measurements, mechanistic information can be inferred in a number of instances.

1. Introduction

The chemistry of methylene (CH_2) is of considerable interest. Being the simplest carbene, CH_2 is amenable to theoretical study and is thus a prototype for this important class of organic intermediates.[1] Furthermore, CH_2 plays a role in a number of chemical systems, particularly combustion and flames.[2] Direct kinetic measurements of CH_2 in the gas phase have been performed over the past decade, focusing primarily on the metastable singlet state ($\tilde{a}\ ^1A_1$, abbreviated $^1CH_2$) because of the ease by which this state may be observed by techniques such as laser-induced fluorescence (LIF) and laser resonant absorption (LRA).[3−21] Few direct studies have been performed on the ground triplet state ($\tilde{X}\ ^3B_1$, abbreviated $^3CH_2$) because of its relative experimental inaccessibility.[22] It is known that the reaction rates for $^1CH_2$ are significantly greater (by typically 6 orders of magnitude at ambient temperature) than they are for $^3CH_2$.[23]

Removal rate constants have been reported for $^1CH_2$ with a range of inorganic species,[5,6,10−14,16,18−20] including water[10,14] and ammonia.[11a] Extensive data also exist for $^1CH_2$ removal by hydrocarbons, including saturated,[5−7,16−18] unsaturated,[8,9,12,16-18] and aromatic[8,9,16,18] species. However, there are few studies of reactions with organic species containing specific functional groups. Wagner's group has measured removal rate constants for methanol,[11a] methyl amine,[11a] and hydrogen cyanide.[12] We have recently presented the results of measurements of removal rate constants for halogen-containing organic species[21] and for selected oxygen-containing organic species.[14,17]

This paper presents the results of an extensive investigation of the removal rate constants for $^1CH_2$ with oxygen-containing organic species. Thirty-seven reactants have been investigated, of which 27 have not been previously studied. Ten of the reactants have been studied by us previously; however, improvements to the experimental system have led to improved reliability of the rate constants measured,[18] and this has motivated us to remeasure the rate constants for these species. The reactants studied include species from the major oxygen-containing organic functional groups, *viz.*, alcohols, aldehydes, ketones, carboxylic acids, esters, ethers, and carbonates. No data were obtained for peroxides.

The list of reactants studied is deliberately extensive so that trends can be established by virtue of sufficient data. The aim of the work has been to provide sufficient data to allow an analysis of the effects on $^1CH_2$ reaction rates of different types of functional groups, different arrangements of functional groups (*e.g.*, straight chain versus cyclic ethers), and different combinations of functional groups. These data provide insights into probable reaction mechanisms.

The technique of laser flash photolysis/laser absorption is used to determine ambient temperature (298 ± 2 K) $^1CH_2$ removal rate constants for these reactants. We are restricted to measuring removal rate constants rather than reaction rate constants in this type of experiment because collision-induced intersystem crossing (CIISC) to $^3CH_2$ competes with reaction. However, it will be argued that in general the removal rate is dominated by the reaction rate for these species, and a difference in removal rate largely reflects a difference in reaction rate.

2. Experimental Section

The apparatus and techniques have been described in detail previously.[14,17,18,20] Briefly, $^1CH_2$ is prepared by the photodissociation of ketene (CH_2CO) using an excimer laser at $\lambda = 308$ nm. The $^1CH_2$ concentration is followed as a function of time by monitoring its absorption with an argon-ion pumped ring dye laser tuned to the $4_{04}(0,14,0) \leftarrow 4_{14}(0,0,0)$ rovibronic transition at 16 928.79 cm^{-1} (vac).[24,25] The signal/noise ratio (S/N) is enhanced with a multipass dual-beam arrangement. The probe and reference beams are directed to identical photodiodes and the signals differentially amplified, with the differential output signal collected by a digital oscilloscope. The oscilloscope averages 256 decay curves to further enhance the S/N level, and the averaged signal is transferred to a laboratory computer. At each reactant pressure, three such averaged traces were collected. After fitting each of these traces, an average

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of the pseudo-first-order rate constants was obtained to further improve the reliability of the data.

The major improvements to the apparatus since our earlier work[14,17] have been the use of an improved differential amplifier and the use of mass flow controllers (MFCs) for introducing the reactant gases into the cell.[18] In the earlier experiments,[14,17] the precursor, bath, and reactant gases were premixed in a bulb to the required partial pressures. The mixture was then flowed continuously via manual control of a needle valve. This procedure was very time-consuming and subject to relatively large errors and limited the field of investigation to reactants that did not react with CH_2CO during premixing (*e.g.*, we were unable to study the reaction of $^1CH_2$ with allyl alcohol[14]). These problems have been rectified by the introduction of mass flow control, and we have now determined $^1CH_2$ removal rate constants for those substrates (allyl alcohol and carboxylic acids) which are known to react with CH_2CO. Separate checks on the reaction between each of these substrates and CH_2CO showed the rates to be insignificant under the experimental conditions. Each of the three gases (N_2, CH_2CO, and the reactant, R) is infused directly from its individual source through a MFC and then into the reaction cell through ports at either end of the cell. N_2 is present in large excess to thermally equilibrate $^1CH_2$.[14,17] The gas mixture is pumped out through a port in the middle of the cell. Thus, the mixing time between R and CH_2CO prior to photolysis is minimized. The input ports are positioned as close as practicable to the windows so that the flow of gases helps to alleviate the buildup of product on the windows, which causes a deterioration in the signal. Pressures were measured with an MKS Baratron type 122A absolute pressure transducer (0−10 Torr) attached directly to the cell.

Liquid reactants (H_2O (demineralized), CH_3OH (Ajax, 99.8%), C_2H_5OH (99.5%), n-C_3H_7OH (Ajax, 99.9%), $CH_3CH(OH)CH_3$ (BDH, ≥99.5%), $CH_3CH(OH)C_2H_5$ (Unilab, 99.8%), CH_2CHCH_2OH (M&B, >97.5%), CH_3OCH_3 (>99%, prepared via refluxing of sodium methoxide and methyl p-toluenesulfonate in methanol), $CH_3OC_2H_5$ (prepared via refluxing of sodium ethoxide and methyl o-toluenesulfonate in ethanol), $C_2H_5OC_2H_5$ (Merck, >98%), c-CH_2CH_2O (Aldrich, >99.5%), c-$CH_2CH_2CH_2O$ (Aldrich, 97%), c-$CH_2C(CH_3)HO$ (Aldrich, 99%), c-$CH_2CH_2OCH_2CH_2$ (Mallinckrodt, 99.99%), $C_2H_5OCHCH_2$ (Aldrich, 99%), $CH_3OCH_2OCH_3$ (Hopkins & Williams), H_2CO (prepared as described in ref 26), CH_3CHO (BDH, 99.0%), C_2H_5CHO (BDH, ≥95%), n-C_3H_7CHO (BDH, ≥98%), CH_3COCH_3 (BDH, >99.5%), $CH_3COC_2H_5$ (Fluka, ≥99.5%), $CH_3CO(n\text{-}C_3H_7)$ (Fluka, >99%), $C_2H_5COC_2H_5$ (Fluka, 99%), $C_2H_5COCHCH_2$ (Aldrich, 97%), $CH_3COCH_2COCH_3$ (BDH, ≥99%), $CH_3COCOCH_3$ (Merck, >98%), HCOOH (Merck, >98%), CH_3COOH (BDH, >99.7%), $HCOOCH_3$ (Unilab, ≥98%), $HCOOCH_2CH_3$ (Fluka, >95%), $HCOO(n\text{-}C_3H_7)$ (Aldrich, 97%), CH_3COOCH_3 (Fluka), $CH_3COOC_2H_5$ (Ajax, ≥99%), $C_2H_5COOCH_3$ (BDH), and $CH_3OCOOCH_3$ (Aldrich, 99%) were degassed using several freeze−pump−thaw cycles and were used without further purification. The gaseous reactant, CH_3OCHCH_2 (Matheson, CP), was used directly as supplied. CH_2CO was prepared by pyrolysis of acetic anhydride ($CH_3COOCOCH_3$)[27] and purified to >99% (determined by IR spectroscopy[28,29]).

3. Results

Rate constants for the removal of $^1CH_2$ were obtained by analysis of the time-dependent absorption data. CH_2CO, N_2, and R each remove $^1CH_2$. Under pseudo-first-order conditions (when R, CH_2CO, and N_2 are in excess relative to the $^1CH_2$ concentration)

$$[^1CH_2]/[^1CH_2]_0 = \exp(-k_{1st}t) \qquad (1)$$

where k_{1st}, the pseudo-first-order rate constant, is given by

$$k_{1st} = k_1[R] + k_2[CH_2CO] + k_3[N_2] \qquad (2)$$

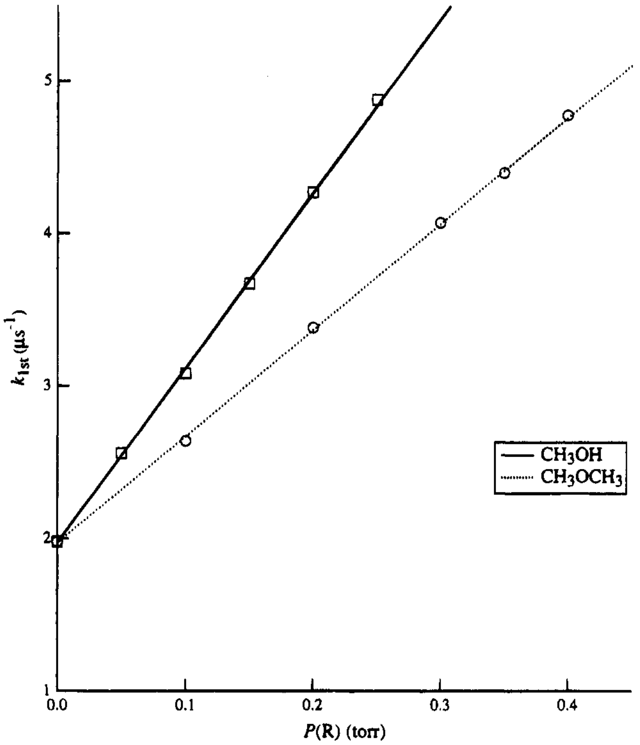

Figure 1. Pseudo-first-order rate constants for $^1CH_2$ removal by CH_3OH (□) and CH_3OCH_3 (○) versus reactant pressure. The size of the symbols is indicative of the uncertainties in the rate constants. The linear least-squares fits represent the removal rate constants given in Table 1.

Although the decay is a single exponential, it is preceded by a fast exponential rise (~50 ns) due to both the response time of the differential amplifier and rotational relaxation of the hot nascent $^1CH_2$.[14] The experimental time-dependence curves were therefore fitted to biexponential functions, although under the experimental conditions employed biexponential fitting yields pseudo-first-order rate constants which are not significantly different from those obtained using a single-exponential fit to the decay, since the rise time is considerably shorter than the decay time. Typical experimental curves and the fits to these curves have been shown previously.[17,18] Removal rate constants for $^1CH_2$ were obtained by weighted linear least-squares fitting of eq 2 using decay rates obtained with a N_2 pressure of 4.0 Torr and a CH_2CO pressure of 0.07 Torr. Reactant pressures were varied from 0.01 to 0.64 Torr, with the upper limit imposed by fast removal rates. Typical plots are shown in Figures 1 and 2. The absolute removal rate constants, k_1, obtained in this work are summarized in Table 1.

The errors quoted correspond to 2σ statistical errors from the weighted linear least-squares analysis plus calculated uncertainties in flow rates and total pressure from manufacturer's specifications. In general those removal rate constants with high percentage errors are associated with relatively nonvolatile reactants. This low volatility leads to increased uncertainty because only low flow rates can be achieved, leading to increased uncertainties in flow rate and partial pressure since the flow controller is operating near its lower limit. In addition,

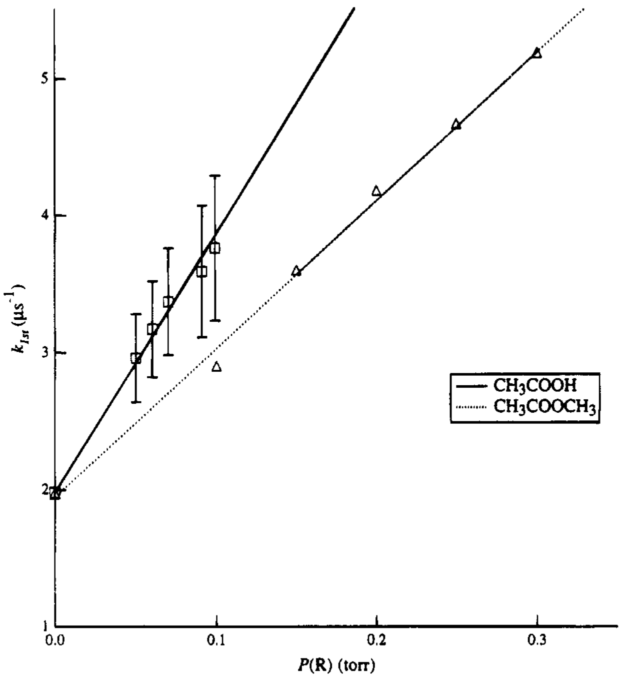

Figure 2. Pseudo-first-order rate constants for $^1CH_2$ removal by CH_3COOH (□) and CH_3COOCH_3 (○) versus reactant pressure. The size of the symbols is indicative of the uncertainties in the rate constants. The linear least-squares fits represent the removal rate constants given in Table 1.

the pressure range over which the removal rates can be measured is limited. Our experience has been that, in cases where higher pressures can be accessed, the trend is for the removal rate constants to change very little, but for the calculated error to reduce considerably. Thus, we actually have higher faith in the rate constants than the usual statistical analysis of errors leads us to report in Table 1 for the low-volatility reactants. We suggest that the 5−10% error found for the high-volatility reactants is a more realistic estimate of the uncertainties involved for all reactants.

4. Discussion

4.1. Removal Efficiencies. In comparing the intrinsic ability of the species studied to remove $^1CH_2$, the rate constants must be scaled to account for the different masses, sizes, and velocities of these species. We scale the removal rate constants to the Lennard-Jones collision rate constant, k_1^{LJ}. The resulting ratios of the removal rate constant, k_1, compared to k_1^{LJ}, for $^1CH_2$ with the same reactant are included in Table 1. They are referred to as "removal efficiencies" throughout this work. The values for k_1^{LJ} were calculated using the method discussed by Troe[30] with the Lennard-Jones parameters taken from Reid et al.[31] or, if unavailable, estimated from the critical volumes and critical temperatures using the method of Chung et al.[32] The Lennard-Jones parameters for $^1CH_2$ were assumed to be the same as those for CH_4.

The results show that $^1CH_2$ is removed with near-collisional efficiency by most reactants. Removal efficiencies typically lie in the range 0.6−0.7 for efficiently removed species. There are few species for which the removal efficiencies exceed this range, the most notable being the two carboxylic acids, formic acid and acetic acid. This magnitude for the removal efficiencies was also typical of the limiting values attained by the halogen-containing organic compounds studied by us previously.[21] It thus appears that, with a few exceptions, removal efficiencies in the 0.6−0.7 range represent limiting values. It is probable that this limit arises from the encounter frequency.

TABLE 1: Comparison of Measured Removal Rate Constants and Lennard-Jones Collision Rate Constants, k_1 and k_1^{LJ} ($\times 10^{-10}$ cm^3 molecule^{-1} s^{-1}) Respectively, for $^1CH_2$ with Oxygen-Containing Organic Species and with H_2O

reactant	k_1	k_1/k_1^{LJ}
Alcohols		
CH_3OH	3.54 ± 0.19	0.64
C_2H_5OH	4.08 ± 0.24	0.69
n-C_3H_7OH	3.88 ± 0.60	0.60
$CH_3CHOHCH_3$	4.36 ± 0.34	0.68
$CH_3CHOHC_2H_5$	3.23 ± 0.70	0.47
CH_2CHCH_2OH	4.73 ± 0.48	0.75
Ketones		
$CH_3(CO)CH_3$	3.95 ± 0.19	0.62
$C_2H_5(CO)C_2H_5$	4.65 ± 0.42	0.63
n-$C_3H_7(CO)CH_3$	4.10 ± 0.40	0.58
$C_2H_5(CO)CH_3$	4.07 ± 0.25	0.60
$CH_2CH(CO)C_2H_5$	4.29 ± 1.37	0.62
$CH_3COCOCH_3$	4.15 ± 0.28	0.61
Aldehydes		
$H(CO)H$	3.02 ± 0.15	0.40
$CH_3(CO)H$	3.52 ± 0.17	0.62
$C_2H_5(CO)H$	3.81 ± 0.20	0.64
n-$C_3H_7(CO)H$	4.40 ± 0.23	0.69
Carboxylic Acids		
$H(CO)OH$	4.74 ± 1.07	0.91
$CH_3(CO)OH$	5.83 ± 1.60	0.97
Ethers		
CH_3OCH_3	2.15 ± 0.11	0.36
$CH_3OC_2H_5$	3.24 ± 0.19	0.52
$C_2H_5OC_2H_5$	4.09 ± 0.20	0.60
CH_3OCHCH_2	3.18 ± 0.16	0.53
$CH_2CHOC_2H_5$	3.76 ± 0.20	0.58
c-CH_2CH_2O	1.93 ± 0.12	0.35
c-$CH_2CH(CH_3)O$	2.97 ± 0.16	0.50
c-$CH_2CH_2CH_2O$	3.92 ± 0.21	0.68
c-$CH_2CH_2OCH_2CH_2$	3.57 ± 0.20	0.57
Esters		
$H(CO)OCH_3$	2.77 ± 0.14	0.48
$H(CO)OC_2H_5$	3.66 ± 0.20	0.58
$H(CO)OC_3H_7$	4.06 ± 0.25	0.59
$CH_3(CO)OCH_3$	3.33 ± 0.16	0.53
$CH_3(CO)OC_2H_5$	3.89 ± 0.23	0.57
$C_2H_5(CO)OCH_3$	3.56 ± 0.26	0.52
Miscellaneous		
$CH_3OCH_2OCH_3$	3.11 ± 0.15	0.51
H_2O	1.86 ± 0.38	0.38
$CH_3(CO)CH_2(CO)CH_3$	3.74 ± 1.28	0.50
$CH_3O(CO)OCH_3$	2.80 ± 0.32	0.43

4.2. Collision-Induced Intersystem Crossing versus Reaction. Because $^3CH_2$ is the ground state, there is the opportunity for CIISC from $^1CH_2$ to $^3CH_2$. The probe laser, tuned to a $^1CH_2$ transition, cannot distinguish CIISC from reaction, since both deplete the $^1CH_2$ population. The rate constants reported here are thus removal rate constants and are equal to the sum of the reaction and CIISC rate constants.

Wagner's group[7−9,11,12] has shown that removal by reaction is the dominant channel for hydrocarbons, accounting for 70−85% of the removal rate constant. Except for CH_3OH, there have been no measurements of the reaction/CIISC branching ratio for oxygen-containing organic species. CIISC accounts for only 13% of the removal rate constant for CH_3OH.[11a] Reaction is even more dominant here than is the case for the hydrocarbons with CIISC clearly being a minor channel.

The most successful model for CIISC in methylene attributes the rate for this process to relaxation within the triplet manifold from states of mixed singlet−triplet parentage.[33,34] Thus, the rate constants for CIISC are largely those for rotational relaxation within the triplet and are relatively insensitive to the collision partner. Consequently, it is difficult to envisage reasons that there should be significant differences among the oxygen-containing organic reactants with regard to their CIISC behavior. It has been suggested that the CIISC efficiencies should scale approximately with the well-depth of the collision partner,[35] and this appears to work reasonably well for ${}^1CH_2$.[7] The CIISC efficiencies predicted from the well-depths for the reactants studied here lie in a restricted range, providing further indication that there should be little difference among them with regard to their CIISC behavior.

In our previous study of halogen-containing organic compounds we found that when CIISC is the only channel available, the removal efficiencies are very low, typically only a few percent of the Lennard-Jones encounter rate.[21] Examination of the data of Wagner and co-workers[7-12] and of Wagener[16] reveals a similar trend: in all cases where CIISC is dominant, small removal efficiencies are observed. Thus, it is found empirically that high removal efficiencies correlate with the case where the removal rate constant is dominated by reaction. The removal efficiencies for all of the organic species studied here are large, suggesting that reaction is dominant in all cases.

In view of the above discussion, when comparing removal efficiencies for these molecules, we assume that the reaction efficiency is the dominant contribution to any difference.

4.3. Comparison with Previous Work. The set of reactants studied includes a number for which there have been different values reported for the removal rate constants. In our initial study[14] we reported removal rate constants for ${}^1CH_2$ with H_2O[10,11b] and CH_3OH[11a] that are respectively 74 and 58% of the values determined by Wagner's group (2.16 ± 0.33 and 3.82×10^{-10} cm^3 molecule^{-1} s^{-1}, respectively).[10,11a] With the improved apparatus used here, we obtain removal rate constants of 1.86 ± 0.38 and $3.54 \pm 0.19 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} for H_2O and CH_3OH, respectively, which are in better agreement with Wagner's findings. These revisions to our reported H_2O and CH_3OH removal rate constants do not alter the general conclusions expressed previously.[14] The CH_3OH removal rate constant reported here agrees with a previous measurement by our group.[17]

Because of improvements in our experimental apparatus, we have also remeasured the removal rate constants for other oxygen-containing species that we have previously studied, *viz.*, C_2H_5OH, n-C_3H_7OH, CH_3OCH_3, CH_3COH, CH_3COCH_3, CH_3COOH, CH_3OCOH, and $CH_3OCOOCH_3$. The revised removal rate constants for these species are largely in agreement with those measured previously; the new values are of higher precision. The only significant change occurs for ethanol,[14] for which the remeasured rate constant is ~50% larger.

We also note that in our original study an attempt was made to study the reaction of ${}^1CH_2$ with allyl alcohol. However, ketene and allyl alcohol reacted significantly during premixing[14] and no ${}^1CH_2$ absorption signal was detected. The present experimental arrangement overcomes this problem, and a removal rate constant for allyl alcohol is reported here.

4.4. Functional Group Comparisons. The data provide the opportunity for a number of comparisons. These include comparisons between molecules with the same functional group but different hydrocarbon chain length or structure (intragroup comparisons) and between molecules with different functional groups (intergroup comparisons). Intragroup comparisons are given first, followed by intergroup comparisons. In making these comparisons, the removal efficiencies are used rather than the removal rate constants (see section 4.1). As discussed above, the removal efficiencies are assumed to be dominated by the reaction channel, and differences in removal efficiencies between reactants are taken to indicate differences in reaction efficiencies.

TABLE 2: Comparison of Removal and Lennard-Jones Collision Rate Constants, k_1 and k_1^{LJ} ($\times 10^{-10}$ cm^3 molecule^{-1} s^{-1}) Respectively, for ${}^1CH_2$ with Alkanes[18]

reactant	k_1	k_1/k_1^{LJ}
CH_4	0.79 ± 0.03	0.16
C_2H_6	1.83 ± 0.10	0.33
C_3H_8	2.23 ± 0.11	0.37
n-C_4H_{10}	3.17 ± 0.15	0.48
i-C_4H_{10}	2.53 ± 0.11	0.38
n-C_5H_{12}	3.35 ± 0.24	0.47
c-C_3H_6	1.63 ± 0.08	0.29
c-C_6H_{12}	3.77 ± 0.21	0.53

Comparisons of the magnitudes of the removal efficiencies among reactants possessing similar functional groups are taken to provide an indication of similarities or differences in the reaction mechanism.

4.4.1. Intragroup Comparisons. In comparing reactants within a group, comparisons are also made with the corresponding alkane in order to provide an indication of the effect of the oxygen-containing functional group on the removal efficiency. The removal rate constants for the alkanes needed for these comparisons are listed in Table 2. The various groups are discussed sequentially below. There are limited data concerning the reaction mechanisms for the functional groups studied. Data are available only for the ethers, ketones, and alcohols.

Alcohols. The alcohols studied were methanol, ethanol, n-propanol, 2-propanol, 2-butanol, and allyl alcohol. They typically display removal efficiencies in the range 0.6–0.7. The exceptions are 2-butanol, which displays a removal efficiency that is somewhat smaller (0.47), and allyl alcohol, which has a somewhat larger value (0.75).

A large efficiency for allyl alcohol is expected, since it is known that the inclusion of double bonds increases the removal rate constant in hydrocarbons by providing the additional reaction pathway of addition across the double bond.[18] This additional pathway is also available when double bonds are present in the alkyl chain of an alcohol. Allyl alcohol and n-propanol differ only by the presence of the double bond in the former. It can be seen that the presence of the double bond has increased the removal efficiency for allyl alcohol by 25% over that for n-propanol. A removal efficiency of 0.75 puts allyl alcohol at the upper extremity of the range of removal efficiencies observed in this study.

The reason for the smaller removal efficiency in the case of 2-butanol appears related to the increasing hydrocarbon component of the molecule. In comparison with the alkanes, short-chain alcohols generally remove ${}^1CH_2$ with considerably higher efficiency. As the alkane chain length increases, the alcohol and alkane removal efficiencies become comparable. For example, methanol has a removal efficiency 4 times that of methane, ethanol is 2.1 times ethane, n-propanol and 2-propanol are 1.6 and 1.8 times propane, respectively, and 2-butanol and n-butane have essentially identical efficiencies.

While there is unfortunately only a single datum, the n-propanol/2-propanol comparison suggests that the position of the OH group may have a small influence on the removal efficiency. The removal efficiency for 2-propanol is 13% higher than that for n-propanol. Although the values overlap within the reported $\pm 2\sigma$ experimental error, this error estimation is rather generous and the raw data suggest that there is in fact a small difference between the two. Both of these species show low volatility, and hence there is relatively large absolute uncertainty associated with their removal rate constants (see the Results section). The raw data suggest that had a larger pressure range been accessible, which would reduce the reported uncertainty, the difference between the removal efficiencies would lie outside the experimental error.

The large efficiencies observed for alcohols compared with alkanes suggest that reaction involves the O−H bond. A discussion of reaction mechanism is deferred until the section dealing with intergroup comparisons.

Ketones. Six ketones were studied. Variations included in this list of compounds are stepwise extension of the hydrocarbon chain length, variation of the position of the C=O group along the alkyl chain, the inclusion of a carbon−carbon double bond, and the inclusion of a second C=O group. These variations had essentially no influence on the removal efficiencies. The removal efficiencies for all ketones studied are ~0.60. This represents an increase from the values for the corresponding alkanes, but as for the alcohols, the difference diminishes with increasing alkyl chain length because of the increased efficiency of the alkanes with increasing chain length.

The data suggest a reaction mechanism involving the carbonyl group since the removal efficiencies are larger than the alkanes. To the best of our knowledge there are no product data for gas-phase reactions of $^1CH_2$ with ketones. However, Bradley and Ledwith[36] have studied the reaction of $^1CH_2$ with CH_3COCH_3 in solution. These authors find that reaction involving C−H insertion is 15 times less likely than reaction involving the C=O group. All products observed could be explained by attachment of $^1CH_2$ to the oxygen atom, forming the $Me_2C{-}O{-}CH_2$ complex, followed by rearrangement or bimolecular reaction. The dominant unimolecular product could also arise through direct attack and insertion at the carbonyl double bond.

In solution, two unimolecular channels involving the carbonyl group were observed.[36] The dominant process leads to the formation of the C=O insertion product 1,2-epoxy-2-methylpropane. This can occur via rearrangement of the $Me_2C{-}O{-}CH_2$ complex (mechanism I) or by direct insertion into the C=O double bond (mechanism II). The second, and relatively minor, unimolecular channel involves addition of $^1CH_2$ to the oxygen atom, again forming the $Me_2C{-}O{-}CH_2$ complex, followed by a shift of a β-hydrogen to the methylene group to create 2-methoxypropene (mechanism III). Our rate measurements for the ketones alone cannot provide insight into whether the relative importance of these two pathways remains the same in the gas phase.

Aldehydes. Four aldehydes were studied, with the only difference being the length of the (saturated) straight alkyl chain. The removal efficiencies are large (in the range 0.62−0.69) with the exception of formaldehyde, for which the removal efficiency is 0.40. The removal efficiencies for the aldehydes are again larger than those for the corresponding alkanes. For example, the removal efficiency of acetaldehyde compared with ethane is 0.62 versus 0.33.

All of the aldehydes, including formaldehyde, can react with $^1CH_2$ to form C=O insertion products via mechanisms I and II. Formaldehyde is, however, alone in being unable to react via mechanism III. It alone also has a removal efficiency well below 0.6. This suggests that the C=O insertion mechanisms (I and II) are not as dominant in the gas phase compared with mechanism III as they were observed to be in solution.

Carboxylic Acids. Only two carboxylic acids were studied, formic acid and acetic acid. Low vapor pressures prevented other reactants in this series from being studied using our present apparatus. They also lead to large reported errors for these species. Both carboxylic acids show very large removal efficiencies, close to unity: they are the largest removal efficiencies observed for any of the reactant series that we have studied. These removal efficiencies are considerably larger than those for the corresponding alkanes (methane 0.16 versus formic acid 0.91; ethane 0.33 versus acetic acid 0.97). A discussion of possible mechanisms responsible for these large removal efficiencies is given below in the comparisons between functional groups.

Ethers. Two types of ethers have been studied, one involving the oxygen as a part of a ring structure and the other with the oxygen in a straight chain. We first make comparisons with compounds within each type of structure and then compare across the structures.

Five straight chain ethers were studied. Of these, three were saturated, with the remaining two containing a lone carbon−carbon double bond. For these three saturated species, a significant increase in removal efficiency is found with increasing length of the alkyl chains. Dimethyl ether has a removal efficiency of only 0.36, whereas for methyl ethyl ether the value is 0.52 and for diethyl ether it is 0.60. The presence of the ether group nevertheless slightly increases the removal efficiencies relative to comparable hydrocarbons. The corresponding hydrocarbons are taken as those with the same number of C−H bonds, because reaction is expected to proceed predominantly by C−H insertion.[37−40] Thus, dimethyl ether is compared with ethane, methyl ethyl ether with propane, and diethyl ether with *n*-butane. The removal efficiencies for the straight chain alkanes are 0.33, 0.37, and 0.48 (ethane, propane, and *n*-butane, respectively), while for the ethers they are 0.36, 0.52, and 0.60 (dimethyl, methyl ethyl, and diethyl ether, respectively). Most interestingly, differences between the alkanes and ethers increase with increasing alkyl component in the ether. This is opposite to the trend found for the alcohols, ketones, and esters (see below) and suggests that there is an additional mechanism operating for the longer chain ethers.

A number of mechanisms are possible for $^1CH_2$ with linear ethers. The simplest are direct insertion into C−H or C−O bonds. The dominant product is consistent with direct insertion into the C−H bond.[37−40] Isotopic labeling experiments have shown that direct insertion into the C−O bond does not occur, at least for diethyl ether.[37] Frey and Voisey[38] have found for longer alkyl chains a small amount of product that could be formally written as an insertion into the C−O bond. However, from the change in the amount of these products in the presence of O_2 these authors suggested that the "insertion" actually proceeds by $^1CH_2$ attack on the oxygen atom, followed by cleavage of the $O{-}CH_3$ bond and then radical combination.[38]

Product analysis reveals that there is another mechanism operating for the longer chain ethers. It has been found that $^1CH_2$ attack at the oxygen atom leading to the intermediate methylenedialkyloxonium ylide and subsequent formation of an ether and an alkene (ethene in the case of ethyl ethers) can also occur. For simplicity, we refer to this as mechanism IV. This process appears to be most important for ethyl ethers in both solution[39] and the gas phase.[38] Product analysis for methyl ethyl ether by Frey and Voisey[38] showed ~3% of the reaction proceeding by this route. However, a gas-phase relative rate measurement by Mehta[40] places mechanism IV at 0.14 of the rate for direct insertion into a C−H bond in diethyl ether, which corresponds to ~12% product formed via this mechanism.

In the situation where reaction proceeds by C−H insertion, one would anticipate that the ether removal efficiencies will correlate well with those of alkanes with the same number of C−H bonds. We have shown above that for dimethyl ether there is very good agreement with the ethane removal efficiency; however, this agreement does not continue for methyl ethyl ether and diethyl ether. The size of the increase in removal efficiencies for the ethyl ethers compared with the alkanes suggests that, in terms of initial removal of $^1CH_2$, mechanism IV cannot be as small as the data of Frey and Voisey suggest[38] and may well be more important than is suggested by Mehta's data.[40] We note that there is no evidence from product analysis for an alternative mechanism to explain this effect.

In contrast to the situation with the alcohols, inclusion of a double bond in the alkyl side chain in the ethers has little effect on the removal efficiency. Comparing methyl vinyl ether with methyl ethyl ether shows that they have virtually identical removal efficiencies (0.53 and 0.52, respectively), and a comparison between ethyl vinyl ether and diethyl ether shows very similar values (0.58 and 0.60, respectively). This is further evidence for the presence of an additional mechanism in the ethyl ethers. The presence of the double bond in methyl vinyl ether removes the possibility of mechanism IV for this species. For ethyl vinyl ether the presence of the double bond removes the possibility of mechanism IV for that end of the molecule. While reducing the possible reaction pathways via mechanism IV, the addition of the double bond simultaneously adds the possibility for attack at this site. The fact that the vinyl and ethyl ethers show essentially identical removal efficiencies suggests that the loss of mechanism IV is compensated for by the addition of the vinyl double bond.

The four cyclic ethers display interesting trends. Three form a progression of increasing ring size (from three- (ethylene oxide) to four- (trimethylene oxide) to five-membered (tetrahydrofuran) rings); the remaining one, propylene oxide, has a three-membered ring with a methyl group attached to the ring. The removal efficiencies for the three ring-only ethers peak at the four-membered ring. They are 0.35 for ethylene oxide, 0.68 for trimethylene oxide, and 0.57 for tetrahydrofuran. Trimethylene oxide and propylene oxide are isomers and have the same number of C−H bonds. The former has a four-membered-ring configuration, whereas the latter has a three-membered ring with a methyl group attached. These two isomers have quite different removal efficiencies: trimethylene oxide has a removal efficiency 36% higher than propylene oxide. In comparing the cyclic and straight chain ethers, one finds little difference in the removal efficiencies of molecules with the same number of carbon atoms, with the sole exception of trimethylene oxide. It is clear that the removal efficiency for this four-membered cyclic ether is unusually large.

The reason for this is not immediately apparent. Mechanisms analogous to those available to the straight chain ethers can be proposed for the cyclic ethers. In addition, it has been found from product analysis that insertion into the C−O bond is possible in the cyclic ethers.[38] As noted above, this mechanism has not been observed in the linear ethers.[37] One might expect the probability for C−O insertion to increase with ring strain and, hence, be most important for the three-membered rings. Thus, we are as yet unable to rationalize the enhancement in removal efficiency for the four-membered-ring ether.

Esters. Removal rate constants were measured for six esters. The variations in molecular structure studied included varying the chain length on the O atom side of the ester group (methyl, ethyl, and propyl formate; methyl and ethyl acetate) and also on the C=O group side (methyl formate, methyl acetate and methyl propionate). Little difference was found between the removal efficiencies for these different species: the values vary over the limited range 0.48−0.59. Close examination of the data reveals, however, that in all cases where a methyl group is attached to the oxygen the removal efficiencies lie close to 0.50, whereas longer chains attached to the oxygen show increased removal efficiency (~0.58). This can be seen by comparing the removal efficiencies of methyl formate, methyl acetate, and methyl propionate (0.48, 0.53 and 0.52, respectively) with those for ethyl formate, propyl formate, and ethyl acetate (0.58, 0.59, and 0.57 respectively). While the difference is only small (~10−15%), it is present across the range of esters studied, and this suggests that it may indicate a real difference in reactivities. It may be that this indicates a small role for mechanism IV when longer alkyl chains are attached to the oxygen atom.

Once again, the esters show enhanced removal efficiencies compared with the alkanes, but as for the alcohols and ketones, this difference diminishes with increasing alkane chain length.

We are unaware of any product analysis for $^1CH_2$ reacting with esters. However, in terms of proposing potential reaction mechanisms, esters can be considered as a combination of an ether and a ketone. The mechanisms available to both of these functional groups are available here. Aldehydes and ketones in general have higher removal efficiencies than do the ethers, and so one might expect that aldehyde/ketone mechanisms would dominate and lead to removal efficiencies similar to the values for these functional groups. Interestingly, the ester removal efficiencies are marginally smaller than those found for the aldehydes and ketones, and we are unable to rationalize this small reduction.

Miscellaneous Functional Groups. The effect of various combinations of functional groups has been investigated in a series including dimethyl carbonate, dimethoxymethane, and acetylacetone. In discussing this group of compounds we also include acetic anhydride, whose removal rate constant has been reported previously.[17]

This series of reactants provides the opportunity to test mechanisms proposed earlier for individual functional groups. On the basis of our previous discussion, we make the following comparisons.

1. Acetylacetone, which possesses two ketone groups, is predicted to have a removal efficiency of ~0.60. The ketones were all observed to have removal efficiencies of this magnitude, including diacetyl, which also has two carbonyl groups. The experimental value for acetylacetone is 0.50, which is less than predicted. The reaction mechanisms proposed for the ketones are available to this species, and we are unable to suggest the reason for its lower removal efficiency.

2. Dimethoxymethane, which has two ether groups, is predicted to have a removal efficiency between those of dimethyl ether and methyl ethyl ether. While it possesses the same number of C−H bonds as methyl ethyl ether, the mechanism available to the longer hydrocarbon chain ethers (mechanism IV) is maximized for an ethyl chain, which is not present here. We find a removal efficiency of 0.51 for this species, which is broadly in line with expectation, although closer to the value for methyl ethyl ether than we might have anticipated.

3. Dimethyl carbonate provides a means for testing our proposal, based on the removal efficiencies for the aldehydes and ketones, that mechanism III is more important in the gas phase than was observed in solution. Since mechanism III is absent for dimethyl carbonate, it should have a removal efficiency lower than those for the ketones, aldehydes, and esters. It can, however, undergo addition across the C=O bond via mechanisms I and II as well as C−H insertion. In this respect it is similar to formaldehyde. It may also be compared with dimethyl ether, which has the same number of C−H bonds but for which there is no C=O addition channel. Thus, one expects the removal efficiency to be above that for dimethyl ether (0.36), comparable to that for formaldehyde (0.40) (products from attack at the C=O bond dominate C−H insertion

products in acetone, and presumably other ketones, in solution[36]), and below those for acetone (0.62) and methyl acetate (0.53). These predictions appear to be well matched by experiment. The observed removal efficiency for dimethyl carbonate is 0.43. This result reinforces our earlier assertion that the importance of mechanism III is increased in the gas phase compared with solution.

4. Acetic anhydride may be compared with diacetyl, since the difference between the two is an oxygen atom bridging the carbonyl groups in the former which is absent in the latter. Thus, one might expect similar removal efficiencies. However, the presence of the bridging oxygen atom in acetic anhydride provides the opportunity for the longer chain ether mechanism IV, leading to ketene and methyl acetate as products. There is no product analysis to illuminate the relative probabilities of these two mechanisms in acetic anhydride. The removal efficiency of 0.75 for this species, which is larger than the usual value for the ketones of ~0.6, may indicate that this second mechanism is available and contributing to the removal efficiency.

4.4.2. Intergroup Comparisons. Clearly, given the number of different functional groups studied, there are a significant number of intergroup comparisons that can be made. We have chosen to focus on comparisons between three pairs of groups. These are aldehydes versus ketones, where one can examine the difference between RCOH and RCOR′, ethers versus alcohols (ROR′ versus ROH), and carboxylic acids versus esters (R(C=O)OH versus R(C=O)OR′). It can be seen from intragroup comparisons that the tendency is for removal efficiencies to lie within a relatively restricted range for particular functional groups. Consequently, we suggest that in comparing removal efficiencies for different functional groups one may gain some insight into the similarity of possible reaction mechanisms in the groups being compared. As we have pointed out above, there are few data concerning reaction mechanisms for $^1CH_2$ reacting with these functional groups. Such data are conventionally obtained from end-product analysis.

Aldehydes and Ketones. In comparing aldehydes with ketones, one is comparing the effect of a hydrogen atom versus a hydrocarbon chain attached to the carbonyl carbon. In making the comparison, we focus on the three pairs acetaldehyde/acetone ($CH_3(CO)H$ versus $CH_3(CO)CH_3$), propionaldehyde/methyl ethyl ketone ($C_2H_5(CO)H$ versus $C_2H_5(CO)CH_3$), and *n*-butyraldehyde/methyl propyl ketone (*n*-$C_3H_7(CO)H$ versus *n*-$C_3H_7(CO)CH_3$). It can be seen that molecules within each pair differ only in the aldehydic hydrogen being replaced by a methyl group in the ketone. The removal efficiencies for each pair are (0.62; 0.62), (0.64; 0.60), and (0.69; 0.58), respectively. The removal efficiencies for the short-chain aldehyde and ketone are equal. The removal efficiencies for the aldehydes increase slightly with increasing chain length, while those for the ketones decrease slightly, so that they become increasingly different. Given that the reaction mechanisms (I, II, and III) involving attack at the oxygen atom are likely to be the same for aldehydes and ketones (see earlier discussion of these reactants), the reason for this widening difference with increasing chain length is not apparent. If the difference were due to a different reaction mechanism, one would expect it to be largest for the short-chain reactants. The real puzzle here is why the difference should increase as the relative importance of the functional group is reduced by the progressive addition of C−H bonds.

Alcohols and Ethers. As was the case for the previous comparison, the difference between alcohols and ethers lies in a hydrogen atom being attached to the oxygen atom in the former and an alkyl group being attached to it in the latter. In the case of alcohols, there is the opportunity for insertion into the O−H bond, whereas for ethers only C−H insertion is possible. For comparable reactants, we find that the alcohols have larger removal efficiencies than do the ethers. This is illustrated by comparing methanol with dimethyl ether (0.64 versus 0.36) and ethanol with methyl ethyl ether (0.69 versus 0.52). Despite the presence of more C−H bonds in the ethers, the removal efficiencies lie below those for the alcohols. This suggests that reaction in the case of the alcohols involves insertion into the O−H bond to produce the ether.

Product analysis supports this conclusion. It has been found that the O−H bond in alcohols is significantly more reactive than the C−H bonds. For example, in *tert*-butyl alcohol the O−H bond is ~11 times as reactive as the C−H bond.[41] In methanol this factor has been reported as 22 and 33 by different authors.[41,42] Similarly large differences between O−H and C−H are observed for ethanol. Interestingly, this does not correlate with the bond strengths, since the O−H bond is stronger than the C−H bond. In ethanol the values are 436.0 and 389.1 kJ mol^{-1} for the O−H and C−H bonds, respectively.[43] Thus, while there are examples where the bond strengths are indicative of the relative removal efficiency,[20,21] this is not the case here.

It is interesting to note that there is the possibility that the alcohols may react via a mechanism analogous to mechanism IV (see ethers). There have, however, been no reports of products from this type of mechanism in studies of $^1CH_2$ reacting with alcohols.[41,42]

Carboxylic Acids and Esters. Similar to the comparison between alcohols and ethers, the difference between carboxylic acids and esters lies in a hydrogen atom being attached to the oxygen atom in the former and a hydrocarbon chain attached to it in the latter (*i.e.*, R(C=O)OH versus R(C=O)OR′). Analogous to this previous case, the difference is large: the removal efficiencies for the carboxylic acids are considerably greater (by almost a factor of 2) compared with those of the corresponding esters. The removal efficiency for formic acid is 0.91 compared with 0.48 for methyl formate, while for acetic acid the removal efficiency is 0.97 compared with 0.53 for methyl acetate.

This suggests that reaction in the case of the acids involves the O−H group. There are two obvious possible mechanisms involving the O−H group. These are either direct insertion into the O−H bond or a hydrogen shift from the O−H following attachment to the carbonyl oxygen, analogous to mechanism III for the ketones.

While a comparison of the relevant bond strengths might provide evidence for one or both of these mechanisms, our observation for the alcohols is that bond strengths are not necessarily good guides (see above). With this caveat we note that the O−H bond strength in acetic acid is virtually identical to the O−H bond strength in ethanol.[43] Given the large extent of O−H insertion in the latter, the identical bond strengths are suggestive of this also being prominent in the former. The removal efficiency of acetic acid (0.97) is, however, larger than that for ethanol (0.69). This may indicate that mechanism III is also operating in the carboxylic acids. However, the C−H bond strength in acetone is 411.3 kJ mol^{-1},[43] which is less than the value for the O−H bond in acetic acid. If a mechanism analogous to mechanism III for the ketones, involving migration of the hydrogen atom from O−H in place of the hydrogen atom from the α-carbon, was occurring for the carboxylic acids, one might expect it to be rapid only if the O−H bond was weaker than the α-C−H bond. This may be another case where the bond strengths alone are not good indicators of the efficiency of the process.

In the absence of product analysis there is little that can be definitively deduced concerning the reaction mechanism for the carboxylic acids, although the comparison with the esters reveals that whichever mechanism is operative it almost certainly involves the O−H bond.

5. Conclusions

Removal rate constants have been presented for $^1CH_2$ with 36 reactants spanning a range of oxygen-containing organic functional groups and with water. It has been argued that differences in removal efficiencies are largely the result of differences in reaction efficiencies. By comparing the removal efficiencies among species containing a specific functional group, mechanistic information has been deduced. Comparisons of removal efficiencies across functional groups have also provided insight into potential reaction mechanisms.

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