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# Rate Constants for the Reaction of Cl with a Series of $C_4$ to $C_6$ Ketones Using the Relative Rate Method

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Rate constants for the reaction of Cl with eight ketones were measured relative to the rate constant of propane in ∼900 Torr of $N_2$ at ambient temperature. Experiments were carried out in a Pyrex reactor with GC analysis of the consumption of the ketones and propane. Chlorine atoms were generated by irradiation of $Cl_2$ in the initial mixture using a black-light-blue fluorescent lamp. The rate constants determined in these experiments ($10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$) are: butanone (3.8 ± 0.3); 2-pentanone (11.6 ± 1.0); 3-pentanone (8.3 ± 0.7); 2-hexanone (19.4 ± 1.9); 3-hexanone (15.3 ± 1.1); cyclopentanone (10.4 ± 0.9); 3-methyl-2-butanone (6.2 ± 0.5); and 4-methyl-2-pentanone (12.8 ± 1.0). The results for 2-pentanone, 3-pentanone, 2-hexanone, 3-hexanone, 3-methyl-2-butanone, and 4-methyl-2-pentanone are significantly higher (by a factor of 3 for 2-hexanone) than reported in two previous absolute rate studies. The likely explanation for this discrepancy is discussed.

## 1. Introduction

Ketones are an important class of organic compounds, and accurate kinetic data concerning their reactivity toward chlorine atoms are useful to understand the atmospheric chemistry of these compounds.[1] There have been several recent measurements of the rate constants for the reaction of Cl atoms with a variety of ketones (butanone, 2-pentanone, 3-pentanone, cyclopentanone, 2-hexanone, 3-hexanone, 3-methyl-2-butanone, and 4-methyl-2-pentanone) with some but not complete overlap of all of the compounds among the studies. The reactions proceed via hydrogen atom abstraction from the ketone to form HCl and a free radical.

$$\mathrm{Cl} + \mathrm{RCOR'} \rightarrow \mathrm{R(\bullet)COR'} + \mathrm{HCl} \qquad (k_{\mathrm{ketone}})$$

$$\mathrm{R(\bullet)COR'} + \mathrm{Cl_2} \rightarrow \mathrm{RClCOR'} + \mathrm{Cl} \qquad (k_{\mathrm{Cl_2}})$$

In the absence of $O_2$, the alkyl radical reacts with the reactant $Cl_2$ in the initial mixture to form chloroketones and regenerate Cl atoms. One set of measurements was carried out by the relative rate method in which the consumptions of the ketone and a reference compound were measured, providing a determination of the ratio $k_{\mathrm{ketone}}/k_{\mathrm{ref}}$.[1] Four sets of measurements were performed using absolute measurement techniques in which the decay of the Cl atom (formed via flash photolysis of $Cl_2$) in the presence of a large excess of a ketone was monitored spectroscopically.[2−5] It might be expected that these five data sets would provide a clear picture of the rate constants of these reactions. Unfortunately, such is not the case. The absolute rate measurements are not in good agreement with one another, differing by factors of 1.2−3 depending upon the ketone. The relative rate measurements[1] agree within the experimental uncertainties with one set of absolute rate constants[2] but not with the other three. Because of the serious discrepancies between these data sets and because only one set of relative rate measurements has been published, a second set of relative rate measurements is needed to verify the earlier results using this proven method of measuring rate constants.[6] The current relative rate experiments were performed using a different type of reactor, a different experimental technique, and a different reference compound from that of ref 1.

## 2. Experimental Section

The relative rate experiments were carried out in a spherical Pyrex (500 cm$^3$) reactor using gas chromatographic (GC) analysis. The studies were performed using $Cl_2/CH_4/C_3H_8$/ketone mixtures in $N_2$ (UHP) diluent. $CH_4$ and $C_3H_8$ purities were >99.99%; freeze, pump, thaw cycles were performed on the ketones (purities >98%) and $Cl_2$ (purity 99.7%). Methane was used for internal calibration of the GC analysis because it is essentially unreactive toward Cl ($k = 1 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$)[7] relative to the other hydrocarbons in the mixture. Propane was used as the reference compound because it is convenient to measure using the GC technique and because $k_{\mathrm{propane}}$ is well established and independent of pressure.

$$\mathrm{Cl} + \mathrm{C_3H_8} \rightarrow \mathrm{products} \qquad (k_{\mathrm{propane}})$$

Chlorine atoms were generated by irradiation with UV light using a single Sylvania F6T5 BLB fluorescent lamp. After a chosen irradiation time, a portion of the contents of the reactor was removed and analyzed by gas chromatography. The mixture was then irradiated for additional times, and additional analyses were performed.

Because many of the ketones studied have relatively low vapor pressures, some loss of these reactants can occur during

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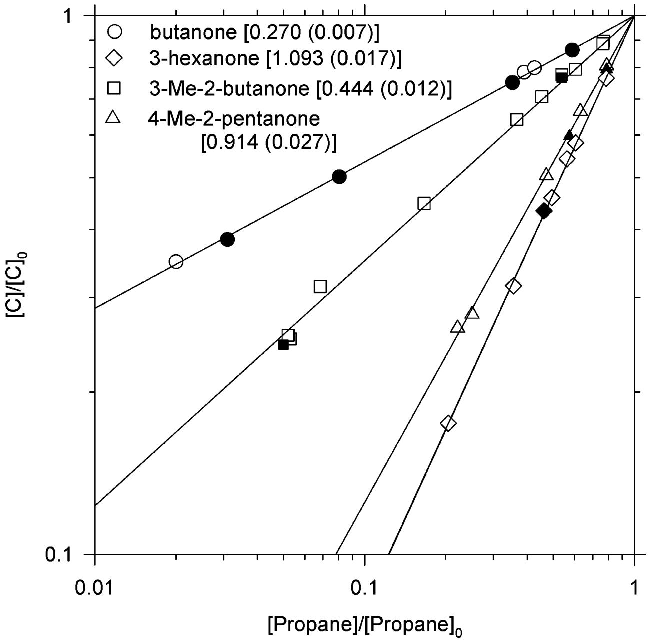

**Figure 1.** Measurement of the rate constants of butanone, 3-hexanone, 3-methyl-2-butanone, and 4-methyl-2-pentanone relative to that of propane at ambient temperature and 800−950 Torr total pressure of $N_2$. Open symbols obtained by sampling reactor contents with a gastight syringe; closed symbols obtained using the GC sample loop (see Experimental Section). Relative rate ratios [$k_{\text{ketone}}/k_{\text{propane}}$] are presented in brackets with 95% confidence limits shown in parentheses for each ketone. Axes are $\log_{10}$ of the measured concentration ratios. [C] = ketone concentration.

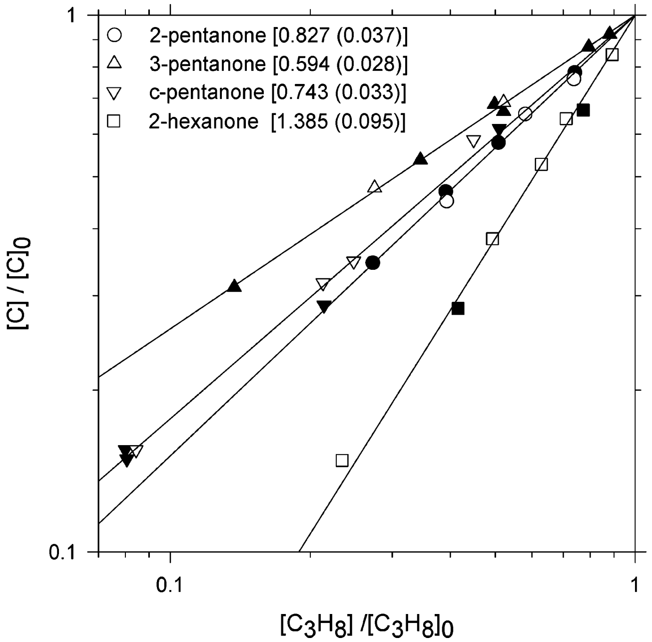

**Figure 2.** Measurement of the rate constants of 2-pentanone, 3-pentanone, cyclopentanone, and 2-hexanone relative to that of propane at ambient temperature and 800−950 Torr total pressure of $N_2$. Open symbols obtained by sampling reactor contents with a gastight syringe; closed symbols obtained using the GC sample loop (see Experimental Section). Relative rate ratios [$k_{\text{ketone}}/k_{\text{propane}}$] are presented in brackets with 95% confidence limits shown in parenthesis for each ketone. Axes are $\log_{10}$ of the measured concentration ratios. [C] = ketone concentration.

the sampling process primarily because of adsorption on tubing during sampling and injection into the GC. The loss is estimated by making a standard mixture of each ketone and comparing the GC/FID signal response to that of propane. To a first approximation the FID response of an organic compound is directly proportional to the number of carbon atoms in the molecule, excluding carbonyl groups that have essentially no response in a FID detector. Thus, butanone is expected to have a signal per unit concentration equal to that of propane. Two different methods of withdrawing sample gas from the reaction flask and injecting it into the GC were used. The first method consisted of filling an evacuated GC sample loop directly from the reaction flask and injecting the sample into the GC via the sample loop. In the second method, samples were taken from the flask by a gastight syringe and injected directly into the heated (373 K) GC injection port, bypassing the sampling system and GC sample loop. For butanone, which has a relatively high vapor pressure at ambient temperature (~90 Torr), the FID response factor was equal to that of propane to within experimental error using both injection techniques. However, for a low vapor pressure ketone such as 2-hexanone (~10 Torr at ambient temperature), the syringe technique gave a response factor 20% lower than propane (corrected for the number of non-carbonyl carbon atoms in the molecule), while the direct injection method showed a response factor 40% lower than propane. Thus, for lower vapor pressure ketones, the syringe method shows a smaller sample loss than does the sample loop injection. For both injection methods, any loss is consistent as shown by the identical results obtained upon repeat analyses of the contents of the reactor both before and after each irradiation and should not affect the determination of the ketone consumption. Also, the consistency of the repeat measurements shows that the ketones are not lost in the flasks during the ~20 min between repeat GC analyses. Both techniques gave identical rate constant ratios even though they show different sample losses for low vapor pressure ketones. This demonstrates that the relative rate results are independent of sampling procedure and, therefore, of any sample loss that may occur.

All experiments were carried out at a total pressure of 800−950 Torr of $N_2$ diluent at ambient temperature (295−297 K). The reactant partial pressures were: $Cl_2$ (100−700 ppm); butanone (69−230 ppm); 2-pentanone (90−230 ppm); 3-pentanone (65−210 ppm); cyclopentanone (23−290 ppm); 2-hexanone (70−140 ppm); 3-hexanone (75−160 ppm); 3-methyl-2-butanone (70−290 ppm); and 4-methyl-2-pentanone (70−220 ppm). For each ketone, the ratio of the partial pressure $Cl_2$/ketone was varied over the range of ~1.5 to ~4. No difference in the rate constant ratios was observed upon variation of the initial reactant partial pressures or the reactant ratio. In addition, for each ketone, an irradiation experiment was performed in the absence of $Cl_2$ to verify that direct photolysis of the ketone does not occur. No photolysis was observed in these experiments.

## 3. Results and Discussion

**3.1. Relative Rate Constant Ratios.** Figures 1 and 2 present log plots of the consumption of the ketone reactants as a function of reference compound (propane) consumption for all relative rate experiments. The open symbols represent data obtained using the gastight syringe sampling technique, while the filled symbols are determined using direct sampling from the reaction flask via the GC sampling loop. As stated above, there is no difference in the data from the two sampling techniques. In addition, varying of the initial reactant concentrations over the ranges presented in the Experimental Section does not affect the measured rate constant ratio. The plots are also linear over

**TABLE 1: Rate Constants Calculated from the Relative Rate Ratios Shown in Figures 1 and 2 (Labeled Current Data)[a]**

| | relative rate ($10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$) | | pulsed laser photolysis ($10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$) | | | |
|---|---|---|---|---|---|---|
| ketone | current data | ref 1 | ref 2 | ref 3 | ref 4 | ref 5 |
| butanone | 3.8(±0.3) | 4.04(±0.33)<br>4.13(±0.57)[b] | 4.08(±0.21) | 3.27(±0.55) | 3.3(±0.2) | 3.24(±0.38) |
| 3-Me-2-butanone | 6.2(±0.5) | | | 4.36(±0.25) | | 7.02(±0.89) |
| 2-pentanone | 11.6(±1.0) | 11.1(±1.0) | 12.3(±1.3) | 4.17(±1.2) | 4.57(±0.28) | |
| 3-pentanone | 8.3(±0.7) | 8.1(±0.85) | 8.87(±0.92) | | 4.5(±0.32) | |
| cyclopentanone | 10.4(±0.9) | | 11.6(±1.2) | | | |
| 2-hexanone | 19.4(±1.9) | 18.8(±1.8) | 20.8(±3.2) | 6.56(±0.98) | 6.54(±0.58) | |
| 3-hexanone | 15.3(±1.1) | 14.3(±1.9) | 14.3(±1.9) | | 6.69(±0.62) | |
| 4-Me-2-pentanone | 12.8(±1.0) | | | 8.44(±0.93) | | 9.72(±1.2) |

[a] Estimated error limits including the error in $k_{\text{propane}}$ are shown in parentheses. Rate constant determinations by other research groups using either relative rate or pulsed laser photolysis with Cl atom measurement are also presented for comparison. [b] This entry was determined from an earlier relative rate measurement with ethane as the reference using the same experimental apparatus as in ref 1.

the wide ranges of the reactant consumption studied. In calculating the rate constant ratios presented in these figures, the curves were forced through the origin because, prior to irradiation, the ratio is by definition unity for both the reference and the ketone ($[C]/[C_0] = 1$). The error limits to the relative rate ratios for each ketone, which are shown in parentheses in Figures 1 and 2, represent 95% confidence limits for each set of data based on least-squares statistical fits to the individual data points for each ketone.

**3.2. Rate Constants Calculated from the Relative Rate Constant Ratios.** Table 1 presents the rate constants determined for the reactions of Cl atoms with the eight ketones whose relative rate constant ratios are presented in Figures 1 and 2 (labeled current data in Table 1). These rate constants are calculated from the rate constant ratios using the known rate constant for $k_{\text{propane}}$ $\{=1.4(\pm 0.1[1\sigma]) \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}\}$.[7] The error limits include the data uncertainties presented in Figures 1 and 2 and the error in $k_{\text{propane}}$ propagated together.

**3.3. Comparison of the Data Sets in Table 1.** Table 1 also contains the rate constants measured for these ketones by other research groups. Based on the data in Table 1, the following observations can be made:

(1) The relative rate constant measurements published in ref 1 agree with the current data to better than 7% in all cases, which is substantially better than the sum of the estimated errors for the two experiments. The pulsed laser photolysis determinations with direct Cl atom detection from ref 2 agree with the current relative rate data and those in ref 1 to within 10% in all cases, again substantially better than the sum of the experimental errors. With the exception of butanone, the rate constants measured in refs 3 and 4 are lower than the current data in all cases by factors of ~1.5 to 3, which is larger than the combined errors. As discussed by Taketani et al.,[1] regeneration of chlorine atoms in the reaction of alkyl radicals with molecular chlorine seems the most likely explanation for the much lower values generally obtained by Cuevas et al.[3] and Albaladejo et al.[4]

(2) The data in ref 5 differ from the current data by less than 25% and agree to within the sum of the error limits for butanone and 3-methyl-2-butanone but not in the case of 4-methyl-2-pentanone. They also do not include measurements of the compounds showing the greatest discrepancy with the relative rate data from refs 3 and 4. A rate constant for cyclopentanone ($=4.76 \times 10^{-11}$) has also been measured[8] using a hybrid (flash photolysis/relative rate) technique, which is substantially lower than the current data and those from ref 2.

## 4. Conclusions

The measurements of the rate constants in the two relative rate experiments (the current data and those of ref 1) cover a very wide range of initial experimental conditions at ambient temperature and pressure, which is important to the verification of the validity of the rate constants. The measurements by Taketani et al.[1] were carried out in either $N_2$ or air diluent with no change in the rate constant ratios. In addition, Taketani et al. used two reference compounds for each ketone. Each ketone was measured relative to $C_2H_4$. They were also measured relative to $C_2H_2$, cyclohexane, or $C_2H_5Cl$, depending upon the rate constant of the ketone in question. The rate constants were independent of the reference compound. In the current measurements, a third reference compound, propane, was used, again giving equivalent results to within experimental error. Finally, the two sets of relative rate data were obtained using different measurement techniques (GC in the present work, FTIR spectroscopy in the previous relative rate study) and reactors with different surface-to-volume ratios (0.6 cm$^{-1}$ in the present work, 0.14 cm$^{-1}$ in the previous relative rate study). These results are confirmed by the absolute rate constant measurements in ref 2. The multiple experiments show that the chemistry in the relative rate experiments is well understood. As discussed in detail elsewhere,[1] it appears that regeneration of chlorine atoms via reaction of alkyl radicals with molecular chlorine was a significant complication in the previous work by Cuevas et al.[3] and Albaladejo et al.[4] leading to a significant underestimation of $k_{\text{ketone}}$.

We recommend that an average of the two extensive sets of relative rate measurements and the absolute rate study of ref 2 will provide the most accurate rate constants available for the reaction of Cl with butanone, 2-pentanone, 3-pentanone, 2-hexanone, and 3-hexanone. Furthermore, because of the unknown source of the discrepancy between the relative rate data and the data in refs 3 and 4, the rate constants determined for 3-methyl-2-butanone and 4-methyl-2-pentanone in the current relative rate experiments are also to be preferred.

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