

## THE RATE OF REACTION OF ACETYL AND BENZOYL RADICALS WITH O<sub>2</sub>

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### Summary

Acetyl and benzoyl radicals were formed by photolyzing acetone, acetylacetone and acetophenone. The radical decays were observed in real time using a photoionization mass spectrometer. Acetylacetone photolysis appeared to form only acetyl + acetyl radicals rather than acetoacetyl + methyl radicals. The photolysis of acetophenone formed both benzoyl + methyl radicals and acetyl + phenyl radicals, with the former split appearing to dominate. The rate constant for the reaction of acetyl radicals with O<sub>2</sub> was determined to be  $(2.0 \pm 0.4) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The reaction between benzoyl and O<sub>2</sub> was faster, with a rate constant of  $(5.7 \pm 1.4) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Both these reactions appeared to be at or near their high pressure limits. Similar measurements were made for acetyl and benzoyl radicals reacting with NO.

### 1. Introduction

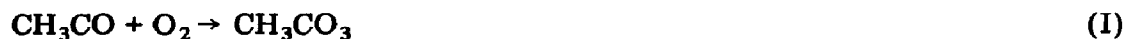
The acetyl radical is an important intermediate in both combustion and air pollution chemistry [1 - 3]. The combustion of many hydrocarbons results in the intermediate formation of acetaldehyde [3]; abstraction of hydrogen from the weak aldehydic bond then forms the acetyl radical. In the polluted troposphere the formation of the lachrymator peroxyacetyl nitrate (PAN) is thought to involve acetyl radicals reacting with O<sub>2</sub> to form acetylperoxy radicals, which can then combine with NO<sub>2</sub> to form PAN [4]. Similarly, benzoyl radicals are thought to be precursors of peroxybenzoyl nitrate, a lachrymator even more powerful than PAN.

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Most of the kinetic work on acetyl radicals has involved stable product analysis [5 - 10]. Although these studies clearly showed that acetyl radicals react with  $O_2$ , the rate constant could only be inferred indirectly, usually as a ratio of rate constants. Only recently has the absorption spectrum of the acetyl radical been observed near 215 nm by flash photolysis kinetic spectroscopy [11].

Previous studies have suggested values for the rate constant for the reaction



ranging from  $10^{-14}$  to  $10^{-13}$   $cm^3$  molecule $^{-1}$  s $^{-1}$  for a variety of temperatures and pressures [5 - 10]. Since all these values are derived indirectly with little agreement between the various studies, we have attempted to measure directly the rate constant for reaction (I). There are no measured or estimated rate constants for the corresponding reaction of benzoyl radicals with  $O_2$ :



## 2. Experimental details

The apparatus and procedures used were identical with those described in a companion study [12]. Acetyl radicals were formed by photolyzing small concentrations of acetone or acetylacetone vapor in 1 - 4 Torr of helium carrier gas. Benzoyl radicals were formed by photolyzing acetophenone vapor. Some of the helium flow swept over the surface of the parent compound held in a low temperature bath, resulting in partial pressures of 10 - 50 mTorr in the reaction cell. A xenon flash lamp was used to photolyze the parent molecules. The lifetime of the flash (about 20  $\mu$ s) was much shorter than the lifetime of the radicals. The absorption spectrum of the parent molecules [13, 14] and the emission spectrum of the flashlamp showed that most of the light absorption occurred in the wavelength range 250 - 310 nm for acetone and 250 - 300 nm for acetylacetone. For acetophenone most of the absorbed light was in the 220 - 260 nm band, but approximately 15% was in the range 260 - 300 nm.

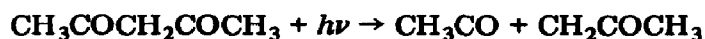
After escaping from the reaction cell through the pinhole, the acetyl and benzoyl radicals were photoionized by radiation from a xenon resonance lamp (8.4 eV per photon) with a sapphire window. The resulting ions were mass analyzed and counted as described previously [12]. The krypton (10.0 eV) and argon (11.4 and 11.6 eV) resonance lines were used when searching for other products. Accumulations of  $10^3$  -  $10^4$  flashes were necessary to give sufficient signal for analysis. The signal counts as a function of time were fitted by a non-linear least-squares method (Curfit program [15]) to a double-exponential equation (eqn. (7) of ref. 12). The resulting value of  $\tau^{-1}$  was interpreted as the rate of pseudo-first-order decay of the radical within the reaction cell.

The acetone (Mallinckrodt), acetylacetone (Matheson, Coleman and Bell) and acetophenone (Matheson, Coleman and Bell) were repeatedly degassed under vacuum and used without further purification. The helium (Liquid Carbonic, 99.998% pure) and oxygen (Liquid Carbonic, 99.995% pure) were taken directly from the tanks using metal tubing and valves.

### 3. Results

Acetyl radicals were observed at  $m/e = 43$  when acetone was photolyzed. This confirms the spectroscopic observation of acetyl radicals by Adachi *et al.* [11] and is in accord with what a generation of photochemists have concluded from indirect measurements [13]. The accompanying methyl radicals were not measured in these experiments although they were observed in the spectroscopic study [11].

When acetylacetone was photolyzed both acetyl radicals and acetonyl radicals were observed:



The acetonyl signal was only about 2% as strong as that of acetyl, probably because of a lower photoionization cross section. This radical is a methyl analog of the vinoxy radical that is currently under intense investigation [16, 17]. No signal could be observed at  $m/e = 85$ , corresponding to the alternate cleavage to methyl and acetoacetyl radicals. When acetophenone was photolyzed both benzoyl radicals and acetyl radicals were observed, the latter being only 10% as strong as benzoyl.

In the absence of another reactant, the acetyl and benzoyl radicals decayed with rates of about  $20 \text{ s}^{-1}$  and  $70 \text{ s}^{-1}$  respectively. These values represent losses due to pump-out from the cell (about  $10 \text{ s}^{-1}$ ), reaction of radicals on the walls and possibly a decomposition reaction. Changes in the parent molecule concentration had no effect on  $\tau^{-1}$ , so that a reaction of the radicals with the parent molecule was not a significant loss process.

When small concentrations of  $\text{O}_2$  or  $\text{NO}$  were added to the system both the acetyl and benzoyl radical decay rates increased. Since the  $\text{O}_2$  and  $\text{NO}$  concentrations were much larger than the radical concentrations, the radical decay should follow pseudo-first-order kinetics

$$-\frac{d[\text{R}]}{dt} = \frac{1}{\tau} [\text{R}] \quad (1)$$

where

$$\tau^{-1} = \tau_0^{-1} + k[\text{O}_2 \text{ or } \text{NO}] \quad (2)$$

Plots of the decay rates as a function of added  $\text{O}_2$  or  $\text{NO}$  are shown in Figs. 1 - 3. The linear correlation observed in these plots confirms the form of eqn. (2) and the slopes give the absolute rate constants. Values of  $k_1$  and  $k_2$

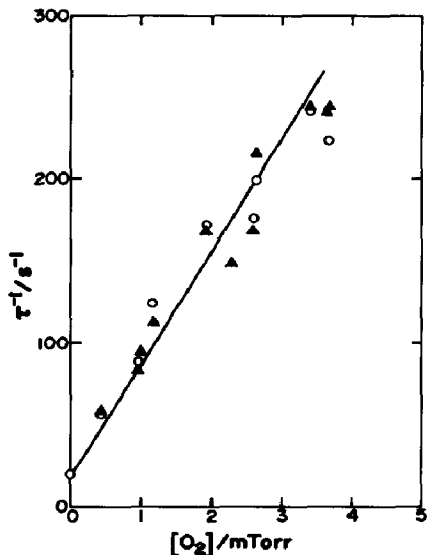


Fig. 1. Decay rates of acetyl radicals as a function of the partial pressure of  $O_2$ : total pressure, 4 Torr; carrier gas, helium; radical precursor, acetone; energy per flash, 12 J ( $\circ$ ) and 6 J ( $\blacktriangle$ ).

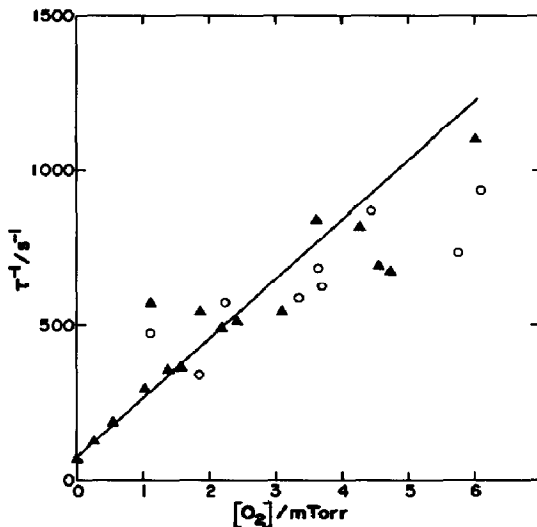


Fig. 2. Decay rates of benzoyl radicals as a function of the partial pressure of  $O_2$ : total pressure, 4 Torr; carrier gas, helium; radical precursor, acetophenone; energy per flash, 10 J ( $\circ$ ) and 5 J ( $\blacktriangle$ ).

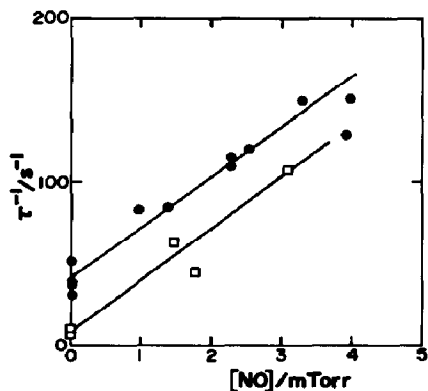


Fig. 3. Decay rates of acetyl and benzoyl radicals as a function of the partial pressure of NO:  $\bullet$ , acetyl radicals generated from acetone in 4 Torr of helium at 10 J per flash;  $\square$ , benzoyl radicals generated from acetophenone in 4 Torr of helium at 5 J per flash. The actual benzoyl decay rates are a factor of 10 greater than the values shown (*i.e.* 75 to 1070  $s^{-1}$ ).

for a variety of conditions are collected in Table 1. The individual values of  $\tau^{-1}$  are recorded elsewhere [18].

#### 4. Discussion

The present experiments give direct evidence that carbonyl radicals are formed in the near-UV photolysis of ketones. Acetone photolyzes to

TABLE 1

Rate constants determined for different experimental conditions

Reaction	Parent compound	Total pressure (Torr)	Flash energy (J)	$k$ ( $\times 10^{-12}$ cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )
CH <sub>3</sub> CO + O <sub>2</sub>	Acetone	4	6	2.1 ± 0.5
	Acetone	4	12	2.1 ± 0.5
	Acetone	1	12	1.9 ± 0.4
	Acetylacetone	4	5	1.6 ± 0.4
	Acetylacetone	1	5	1.4 ± 0.3
C <sub>6</sub> H <sub>5</sub> CO + O <sub>2</sub>	Acetophenone	4	10	5.2 ± 1.2
	Acetophenone	4	5	5.5 ± 1.2
	Acetophenone	2	5	7.6 ± 2.1
CH <sub>3</sub> CO + NO	Acetone	4	10	0.93 ± 0.27
C <sub>6</sub> H <sub>5</sub> CO + NO	Acetophenone	4	5	9.4 ± 3.5

acetyl + methyl radicals while acetophenone forms both benzoyl + methyl and acetyl + phenyl radicals. The absence of photoionization cross sections prevents the assignment of values to the branching ratios. If we assume that all carbonyl radicals have about the same cross section, then the photolysis of acetophenone forms benzoyl + methyl radicals about 10 times more readily than it forms acetyl + phenyl radicals. Similarly, acetylacetone cleaves primarily to acetyl + acetyl rather than to acetoacetyl + methyl.

The measured rate constant for reaction (I) appears to be significantly different for different parent molecules. With acetylacetone as the precursor, the value of  $k_1$  is lower by about 25% than that measured when acetone is the precursor. The reason for this difference is not clear but is probably related to the greater complexity in the acetylacetone system. For example, if the acetyl radicals react with O<sub>2</sub> to form acetyl radicals, the observed decay of acetyl will be slower than it would be without this secondary source of radicals. Because of this possibility the value of  $k_1$  measured with acetone as the parent, *i.e.*  $(2.0 \pm 0.4) \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, is to be preferred. The error limits to  $k_1$  are derived from the scatter of the  $\tau^{-1}$  values (standard deviation of the slope, 2% - 20%), the estimated errors in the absolute O<sub>2</sub> concentrations (8%) and the uncertainty in the data analysis procedure (20%, owing to the choice of  $\tau_p$  [12]). A similar treatment of the benzoyl data yields a value for  $k_2$  of  $(5.7 \pm 1.4) \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Neither rate constant appears to depend on the total pressure within the limited range of 1 - 4 Torr, which means that the reported values are at or near their high pressure limits.

Attempts to observe the products of these reactions by photoionization were unsuccessful. No credible signals with the proper time signature were observed at the masses corresponding to the peroxy radicals; by analogy with the properties of HO<sub>2</sub> and CH<sub>3</sub>O<sub>2</sub> [19, 20], these peroxy radicals are

expected to have low photoionization cross sections and ionization potentials above 10 eV. Acetyl peroxy radicals were observed by Hunziker and Wendt [21] when acetyl radicals were generated in the presence of O<sub>2</sub>.

The reactions of acetyl and benzoyl radicals with NO were studied less extensively. When the limited data were analyzed, the rate constant for acetyl + NO was  $(9.3 \pm 2.7) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and that for benzoyl + NO was  $(9.4 \pm 3.5) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (see Fig. 3).

The present value for  $k_1$  is larger than previous estimates in the literature [5 - 7]. These early studies involved a competition between reaction (I) and the thermal decomposition of the acetyl radical:



The amount of CO produced was taken as a measure of the extent of reaction (III), while reaction (I) was assumed to result in CO<sub>2</sub> formation. The ratio of these products together with the O<sub>2</sub> concentration resulted in a value for  $k_3/k_1$ . The expression for  $k_3$  recommended by O'Neal and Benson [22] was then used to calculate  $k_1$ .

There are two problems with the above procedure. Subsequent studies have questioned the O'Neal and Benson expression for  $k_3$  [23, 24]. Also, Pearson [5] has shown by using <sup>18</sup>O<sub>2</sub> that most of the CO formed in the CH<sub>3</sub>CO + O<sub>2</sub> system is not the result of reaction (III). Consequently, these previous values of  $k_1$  are probably incorrect.

One value for  $k(\text{CH}_3\text{CO} + \text{NO})$  of  $3 \times 10^{-13}$  has been reported [9, 10]. Although this is lower than the value reported in Table 1 by a factor of 3, this agreement is satisfactory considering the indirect method used and the uncertainty in the rate constant of the reference reaction (CH<sub>3</sub>CO + I<sub>2</sub>).

The reaction of the benzoyl radical with O<sub>2</sub> is faster than that of acetyl by a factor of almost 3. This is consistent with the trend observed previously, namely that radicals with a lower ionization potential (IP) react more rapidly [12, 25]. However, the present values for  $k_1$  and  $k_2$  clearly do not fit the approximate linear relationship between ln  $k$  and IP found [25] for the reactions of alkyl radicals with O<sub>2</sub>. For similar IP values, the carbonyl radicals react more slowly with O<sub>2</sub> than do the alkyl radicals. The rationale for the difference between alkyl and carbonyl radicals is not yet clear.

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