Rate Constant for the Reaction of $CH_3C(O)CH_2$ Radical with HBr and Its Thermochemical Implication

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Received 16 February 2005; accepted 14 August 2005

DOI 10.1002/kin.20135

ABSTRACT: The fast flow method with laser induced fluorescence detection of $CH_3C(O)CH_2$ was employed to obtain the rate constant of k_1 (298 K) $= (1.83 \pm 0.12\ (1\sigma)) \times 10^{10}$ $cm^3\ mol^{-1}\ s^{-1}$ for the reaction $CH_3C(O)CH_2 + HBr \leftrightarrow CH_3C(O)CH_3 + Br$ (1, −1). The observed reduced reactivity compared with *n*-alkyl or alkoxyl radicals can be attributed to the partial resonance stabilization of the acetonyl radical. An application of k_1 in a third law estimation provides $\Delta_f H^{\circ}_{298}(CH_3C(O)CH_2)$ values of -24 kJ mol^{-1} and -28 kJ mol^{-1} depending on the rate constants available for reaction (−1) from the literature. © 2005 Wiley Periodicals, Inc. Int J Chem Kinet 38: 32–37, 2006

INTRODUCTION

Recent interest in the kinetic behavior [1–3] and thermochemical properties [4,5] of the acetonyl radical, $CH_3C(O)CH_2$, stems in a great part from the recognition of the important role this radical plays in the chemistry of the atmosphere [6,7]. Acetonyl is formed in OH hydrogen abstraction reaction from acetone [7], $CH_3C(O)CH_3$, which has recently been found one of the most abundant partially oxidized organics in the atmosphere [8].

In this paper, we report a room temperature kinetic study of the reaction of acetonyl radical with HBr (1):

$$CH_3C(O)CH_2 + HBr \leftrightarrow CH_3C(O)CH_3 + Br \quad (1, -1)$$

Motivation for this study has been twofold: as a continuation of our previous work [3] to investigate structure–activity relationships, and to provide an estimation for the heat of formation of the acetonyl radical which has recently become debated in the literature [4,5].

The long-accepted value of $\Delta_f H^{\circ}_{298}$ $(CH_3C(O)CH_2) = -23.0 \pm 7.5$ kJ mol^{-1} originates from a classical "bromination equilibrium" kinetic study published more than 30 years ago by King et al.

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Contract grant sponsor: Hungarian Research Fund OTKA.
Contract grant number: TO37690.
Contract grant sponsor: EU Integrated Project SCOUT-O3.
Contract grant number: GOCE-CT-2004-505390.

[9]. They determined a temperature-dependent rate constant expression for the reaction $Br + CH_3C(O)CH_3$ (−1) from a detailed spectrophotometric investigation of the gas-phase thermal bromination of acetone and derived the abovementioned value of heat of formation. The derivation was based on an assumed reaction mechanism and estimated activation energy for the reaction of acetonyl radical with Br_2. The $\Delta_f H^\circ_{298}$ value by King et al. has essentially been adopted by the different thermochemical data evaluations, such as [10]. Recently, Bouchoux and co-workers [5] reported $\Delta_f H^\circ_{298}$ $(CH_3C(O)CH_2) = -34 \pm 3$ kJ mol^{-1} by results of gas-phase ion thermochemical experiments. Bouchoux et al. also re-evaluated the results of a previous experimental determination by Holmes et al. [11] proposing the revised value of $\Delta_f H^\circ_{298}$ $(CH_3C(O)CH_2) = -31.7 \pm 6.4$ kJ mol^{-1}. Recent high-level quantum chemical computations support the new "low" values supplying −28 kJ mol^{-1} [2], -32 ± 4 kJ mol^{-1} [4], and −36.2 kJ mol^{-1} [5] $CH_3C(O)CH_2$ heat of formation. In view of the large disparity in the reported $\Delta_f H^\circ_{298}(CH_3C(O)CH_2)$ values, we have decided to re-examine the bromination kinetics of acetone by using current experimental techniques. The first results are presented here.

EXPERIMENTAL

The direct kinetic method of low-pressure isothermal fast discharge flow (DF) coupled with pulsed laser induced fluorescence detection (LIF) of acetonyl radicals was used to carry out the experiments. The apparatus and experimental methodology have recently been described in detail [3] and hence only a brief summary is given here.

The flow reactor was a 40.1-mm-i.d. Pyrex tube which was equipped with a coaxially mounted moveable quartz injector to achieve time resolution. $CH_3C(O)CH_2$ radicals were produced in the injector by reacting F atoms with acetone. HBr was introduced in the reactor upstream, through a side arm. In order to diminish the wall loss of acetonyl, the inner surface of the reactor was coated with either halocarbon wax (Halocarbon Corporation, series 1200) or a thin film of Teflon (DuPont, FEP 856-200), in the following abbreviated as HALOWAX and PTFE, respectively. The reaction was monitored by LIF detection of the depletion of the concentration of $CH_3C(O)CH_2$ along the reaction distance. The excitation wavelength of 351 nm was delivered by an excimer-laser (Lambda Physik, EMG 101 MSC). That is, we have made use of our recent observation [3] that the acetonyl radical can be detected with good sensitivity not only with a tunable laser source but also with a fixed-wavelength XeF excimer laser. The laser energy entering the detection volume was about 8 mJ per pulse which provided an acetonyl detection limit of about 8×10^{-15} mol cm^{-3} (at $S/N = 1$ signal-to-noise ratio).

Helium (Linde, 99.996%) was the carrier gas which was passed through liquid nitrogen cooled traps before entering the flow system. Acetone (Aldrich, +99.9% HPLC grade) was degassed by freeze (77 K)–pump–thaw cycles in a vacuum line. HBr (Merck, >99.8%) was further purified by repeated vacuum distillations between bulbs kept at given low temperatures. The purified HBr sample was stored at N_2(l) temperature in dark and was metered into the flow reactor from a container thermostated to 195 K. The Br_2 content of HBr was checked regularly by spectrometric analysis at $\lambda = 400$ nm ($l = 20$ cm optical path). It was found always less than 0.02%. Metal parts were avoided wherever possible to prevent heterogeneous decomposition of HBr.

RESULTS AND DISCUSSION

Rate Constant for the Reaction $CH_3C(O)CH_2 + HBr$ (1)

The experiments were conducted at room temperature ($T = 298 \pm 2$ K) and $P = 2.66 \pm 0.05$ mbar He pressure (errors quoted throughout the paper are 1σ of the measurement precision). Pseudo-first-order conditions were applied with hydrogen bromide in large excess over the acetonyl radical, $[HBr] \gg [CH_3C(O)CH_2]_0 \approx 1.5 \times 10^{-12}$ mol cm^{-3}. The reaction was studied between 8 and 80 ms reaction time corresponding to the fixed flow velocity and the varied distance of the tip of the sliding injector from the detection volume.

The experimental procedure involved the recording of acetonyl fluorescence signals (S) in the presence (on) and absence (off) of the reactant HBr at different positions of the moveable injector ("on–off" technique [12]). The pseudo-first-order rate constant, k'_1 was obtained from

$$-\bar{v}\,\frac{d\ln(S_{on}/S_{off})}{dx} = k'_1 \qquad \text{(I)}$$

where $\bar{v}$ is the average linear flow velocity and x is the varied reaction distance.

Typical semilogarithmic $CH_3C(O)CH_2$ decay plots are shown in Fig. 1 according to Eq. (I). The experimental data obeyed straight lines, the linear-least-squares (LSQ) analysis of which supplied k'_1. In order to test

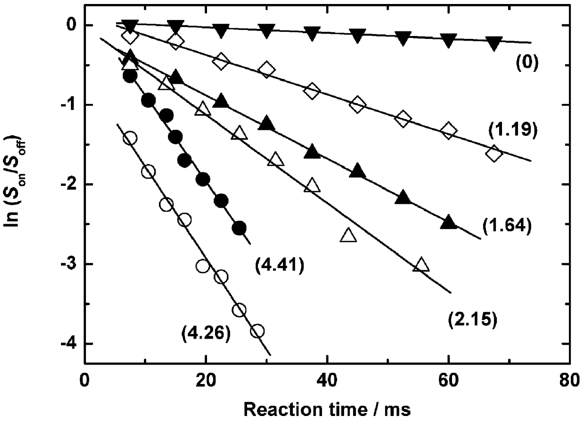

Figure 1 Representative pseudo-first-order decay plots for the reaction of $CH_3C(O)CH_2$ radical with HBr. Empty and full symbols designate experiments carried-out in reactors with PTFE and HALOWAX wall coatings, respectively. The numbers in brackets are HBr concentrations in 10^{-9} mol cm^{-3}.

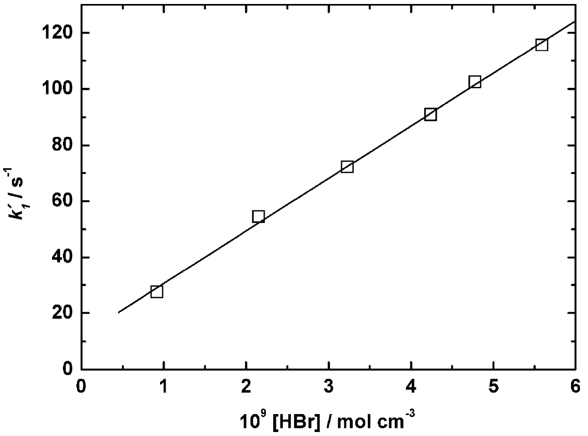

Figure 2 Plot of pseudo-first-order rate constant vs. [HBr] to obtain the bimolecular rate constant for the reaction $CH_3C(O)CH_2$ + HBr (1) in PTFE-coated reactor.

for heterogeneous effects, experiments were performed with both HALOWAX- and PTFE-coated reactors. The obtained pseudo-first-order rate constants are plotted against [HBr] in Figs. 2 and 3. The good straight lines indicate the realization of pseudo-first-order conditions, providing the bimolecular rate constant, k_1, as LSQ slopes. The experimental conditions and kinetic results are summarized in Table I. Note that the $[F_2]_0$ concentrations in Table I are approximately equal to the initial acetonyl concentrations, given the degree of dissociation of F_2 in the microwave discharge (~70%) and an estimated loss of radicals inside the moveable injector. ln S_{off} data as a function of reaction time have also provided straight lines, the slopes of which are

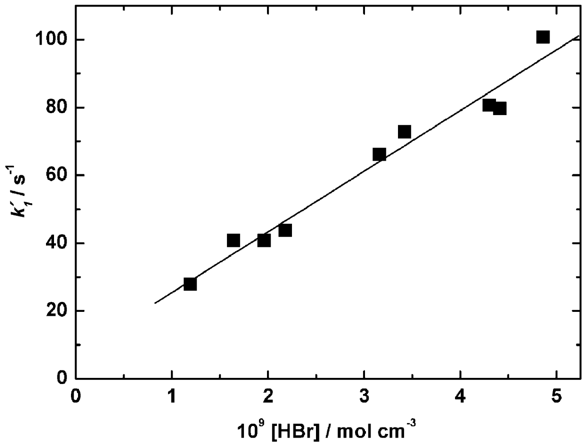

Figure 3 Plot of pseudo-first-order rate constant vs. [HBr] to obtain the bimolecular rate constant for the reaction $CH_3C(O)CH_2$ + HBr (1) in HALOWAX-coated reactor.

the "wall rate constants" in the range of $k_w = 2\text{–}15\ s^{-1}$. The wall consumption of the acetonyl radicals could be accounted for directly by using the "HBr reactant on–off" experimental procedure [12] enabling k_1' values even smaller than the wall rate constants to be determined. In the present work, no correction of the rate constants for diffusional effects and viscous-flow was made. According to our experience with similar systems, these corrections are usually small and tend to cancel each others effect. Although technically the rate constant for the overall reaction has been measured in the experiments, in effect it provides the rate constant for hydrogen abstraction (1), since abstraction of Br by acetonyl is significantly endothermic.

As seen in Table II, the rate constants determined in the two reactors agree within 5%. Thus, we take their average as the recommended rate constant for the reaction between $CH_3C(O)CH_2$ and HBr from the present study given with the larger error margin from the two series of measurements:

$$k_1(298\,\text{K}) = (1.83 \pm 0.12) \times 10^{10} \text{cm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$$

As far as we are concerned, this is the first determination of k_1 reported in the literature.

Assessment of Systematic Errors. One of the potential sources of systematic errors is the Br_2 contamination of HBr. From two survey experimental runs, we have obtained $\sim 5.5 \times 10^{12}$ cm^3 mol^{-1} s^{-1} for the rate constant of the reaction of the acetonyl radical with Br_2. That is, even a small bromine impurity might cause a large overestimation of k_1. As noted, the Br_2 content of HBr entering the reactor was regularly analyzed and was found to be <0.02%. In fact, this upper bound

Table I Summary of Experimental Conditions and Kinetic Results for the Reaction $CH_3C(O)CH_2$ + HBr (1); $T = 298 \pm 2$ K, $P = 2.66 \pm 0.05$ mbar (He)

$\bar{v}$ (cm s^{-1})	$[F_2]_0$[a] ($\times 10^{-12}$ mol cm^{-3})	[Acetone] ($\times 10^{-11}$ mol cm^{-3})	[HBr] ($\times 10^{-9}$ mol cm^{-3})	k'_1 (s^{-1})	No.[b]	($k_1 \pm 1\sigma$) ($\times 10^{-10}$ cm^3 mol^{-1} s^{-1})
463–773	1.05–2.43	3.23–13.5	1.19–4.86	28–101	9	(1.79 ± 0.12)[c]
446–778	0.96–3.60	3.67–8.30	0.92–5.59	28–116	6	(1.87 ± 0.04)[d]

[a] $[F_2]_0 \approx [F]_0 \approx [CH_3C(O)CH_2]_0$.

[b] Number of k'_1 determinations.

[c] HALOWAX reactor coating.

[d] PTFE reactor coating.

Table II Comparison of Rate Constants for the Reactions of Selected Free Radicals with HBr

Reaction(i)	k_i(298 K) (cm^3 mol^{-1} s^{-1})	Reference
$CH_3C(O)CH_2$ + HBr (1)	1.8×10^{10}	This work
CH_3O + HBr (2)	8.4×10^{11}	Farkas et al. [16]
CH_2OH + HBr (3)	4.4×10^{12}	Dóbé et al. [17]
C_2H_5 + HBr (4)	5.6×10^{12}	Seakins et al. [18]
n-C_3H_7 + HB_r (5)	8.5×10^{12}	Seetula and Slagle [23]
C_3H_5 + HBr (6)	1.7×10^{9}	Seetula [19]

corresponds to the detection sensitivity of our spectrometric method and so about 10% overestimation in k_1 cannot be entirely excluded by our measurements. It is more difficult to assess (exclude) the in situ formation of Br_2 on the reactor surface. In the case of a heterogeneous Br_2 formation, one would expect large wall rate constants and the occurrence of some "memory" or hysteresis effect in the course of the experiments. None of these were, however, observed. The best argument against an interfering heterogeneous effect is provided by the very good agreement of the rate constants determined in flow tubes with different wall coatings.

Structure–Activity Relationships

The acetonyl radical contains a partially delocalized electronic structure which may be viewed as a "resonance" between the "alkyl form" $^\bullet CH_2C(=O)CH_3$ and the "alkoxyl form" $CH_2=C(-O^\bullet)CH_3$ mezomeric structures. Recent experimental and theoretical studies [1–3] have shown the acetonyl radical to behave like an alkyl radical and not like an alkoxyl radical in its elementary reactions with O_2, NO, NO_2, and H atoms. In order to further examine structure–activity relations, the rate constant obtained for reaction (1) in the present work has been compared with those for selected radical + HBr reactions from the literature in Table II. As seen, both the carbon-centered radicals CH_3, C_2H_5, n-C_3H_7, and CH_2OH as well as the CH_3O radical react with HBr with rate constants that are not very different from each other, and all are significantly larger than that of the acetonyl + HBr reaction. That is, by the magnitude of k_1, it cannot be decided if the H atom from HBr is abstracted directly by the CH_2 moiety of acetonyl or an "alkoxyl reaction" takes place first to form allylalcohol, $CH_2=C(-OH)CH_3$, which isomerizes then to acetone. An answer to this question might be expected from quantum chemical computations. On the other hand, the relatively low reactivity of $CH_3C(O)CH_2$ toward HBr may be explained by that this radical possesses some degree of resonance stabilization [4]. The correlation of resonance stabilization with low reactivity is supported by the observation in Table II that the strongly resonance stabilized allyl radical [13–15] reacts much slower with HBr than the other free radicals without electron delocalization. The acetonyl radical appears to present an intermediate case, but resembling more the reactivity of the allyl radical, e.g., k_5 (n-C_3H_7 + HBr) : k_1 ($CH_3C(O)CH_2$ + HBr) : k_6 (C_3H_5 + HBr) $\approx 5000 : 11 : 1$ (Table II, $T = 298$ K).

Enthalpy of Formation of $CH_3C(O)CH_2$

The rate constant determined for reaction (1) in the current work enables the estimation of the heat of formation for the acetonyl radical by employing the so-called "third-law analysis" procedure [13,14]. To accomplish this procedure in the present case, the rate constant for the "reverse" reaction Br + $CH_3C(O)CH_3$ (–1) at T = 298 K must also be known.

We are aware of only two kinetic studies of the reaction of Br atoms with acetone [9,21]. King et al. investigated the gas-phase thermal bromination of acetone over the temperature range 494–618 K. From measurements of initial rates of Br_2 consumption, they determined a rate constant expression in the Arrhenius form. An extrapolation of the rate constant expression to room temperature yields k_1 (298 K) = $(6.34 \pm 7.18) \times 10^3$ cm^3 mol^{-1} s^{-1} (with 1σ propagated error).

Very recently, we have performed photobromination kinetic study of acetone employing the relative-rate method coupled with gas-chromatographic product analysis [21]. The rate constant ratio k_{-1}(Br + acetone)/k (Br + *neo*-C_5H_{12}) = 0.50 ± 0.31 was determined at room temperature. This was converted to k_{-1}(298 K) = $(2.73 \pm 1.71) \times 10^4$ cm^3 mol^{-1} s^{-1} by making use of the rate constant expression for the reference reaction Br + *neo*-C_5H_{12} that was determined in a previous direct kinetic study in the temperature range 688–775 K [22]. The two literature rate constants available for reaction (−1) differ by a factor of 4. This large disparity may be due, at least in part, to the long-range extrapolation of the rate constant expressions to room temperature.

An estimation of the $CH_3C(O)CH_2$ heat of formation by the kinetic data requires auxiliary thermochemical quantities as well. Most of them have been taken from [20], which are the following: $\Delta_f H^o_{298}$(HBr) = (-36.29 ± 0.16), $\Delta_f H^o_{298}$(acetone) = (217.1 ± 0.7), and $\Delta_f H^o_{298}$(Br) = (111.87 ± 0.12) kJ mol^{-1} as well as S^o_{298}(HBr) = (198.7 ± 0.01), S^o_{298}(acetone) = (295.46 ± 0.01), and S^o_{298}(Br) = (175.02 ± 0.01) J mol^{-1} K^{-1}. The ab initio computational result of $S^o_{298}(CH_3C(O)CH_2)$ = (298 ± 2) J mol^{-1} K^{-1} by Bouchoux et al. [5] was accepted for the entropy value of the acetonyl radical (the error given is our estimation).

A combination of k_1(298 K) from the current work with the extrapolated k_{-1}(298 K) from King et al. [9] in a third law procedure gives $\Delta_f H^o_{298}(CH_3C(O)CH_2)$ = (-24.3 ± 5.8) kJ mol^{-1}. This datum is close to the "high" heat of formation value long in use for the acetonyl radical (see Introduction).

In contrast with the above result, the third law analysis of k_1(298 K) (this work) and k_{-1}(298 K) [21] provides $\Delta_f H^o_{298}(CH_3C(O)CH_2) = (-28.1 \pm 3.1)$ kJ mol^{-1}. That is, a $CH_3C(O)CH_2$ heat of formation which is in between the previous "high" values and the more recent "low" values reported in the literature (see Introduction).

That is, no conclusive answer can be offered to support either the "high" or "low" $\Delta_f H^o_{298}$ values for $CH_3C(O)CH_2$ by the kinetic information available for the bromination equilibrium reaction of acetone at the present stage. Clearly, a more accurate $CH_3C(O)CH_2$ heat of formation might be expected from temperature-dependent kinetic studies of both reaction (1) and its reverse (−1) by using preferably direct kinetic methods in a wide and at least partially overlapping temperature ranges.

The authors are indebted to Prof. J. Espinosa-García for helpful discussions.

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