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Reaction of Atomic Bromine with Difluorochloromethane. The Heat of Formation of the $CClF_2$ Radical and the $D°(CClF_2–H)$ Bond Dissociation Energy

K. Miyokawa[†] **and E. Tschuikow-Roux***

Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4

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The gas-phase photobromination of $CHClF_2$ (**1**) in the presence of CH_3Cl (**2**) as competitor has been studied in the temperature range 80–150 °C at halomethane pressures of ~35 Torr and a Br_2 pressure of ~2.3 Torr. The temperature dependence of the rate constant ratio is found to obey the Arrhenius expression $\ln (k_1/k_2) = (-0.0885 \pm 0.0580) - (1144 \pm 20)/T$. This result is combined with an earlier relative study of CH_3Cl (**2**) vs C_2H_6 (**3**) and a recent direct determination by kinetic spectroscopy of the rate constant for the bromination of ethane (k_3) to obtain absolute rate parameters for the reaction $CHClF_2 + Br \rightarrow CClF_2 + HBr$. Using a justifiable approximation concerning the magnitude of the activation energy difference for the reverse reactions between any two competitors of similar complexity, and other thermochemical data from the literature, the following quantities have been derived: $\Delta H_f°_{298}(CClF_2) = -66.7 \pm 2$ kcal mol^{-1} and $D°(CClF_2–H) = 100.7 \pm 2$ kcal mol^{-1} where the uncertainties are conservative estimates. On the basis of the new value of k_3, activation energies for the bromination of CH_4 and other halomethanes are reported.

Introduction

There is a growing interest in the physical and chemical properties of hydrochlorofluorocarbons (HCFCs) as alternatives to the widely used chlorofluorocarbons (CFCs). These HCFCs are expected to have a relatively shorter lifetime in the troposphere as they react with hydroxyl to yield chlorofluorocarbon radicals which are then converted to compounds less harmful with respect to ozone depression in the stratosphere.[1] Therefore, it seems relevant to investigate the thermochemical properties of chlorofluorocarbon radicals. Since difluorochloromethane (HCFC-22) is considered to be a prominent candidate among the alternatives to CFC-11 and -12, we report here the kinetics of the photobromination of $CHClF_2$ and thermochemical data for the $CClF_2$ radical estimated from this and other kinetic data.

Experimental Section

With one exception, all chemicals were obtained commercially: $CHClF_2$ and CH_3Cl from Matheson; CH_2BrCl from Columbia Organic Chemicals Co.; and ACS grade Br_2 from Fisher Scientific Co. Prior to their use, all samples were subjected to the usual trap-to-trap distillation and degassing under vacuum at liquid nitrogen temperature until the impurity levels were below the GC detection limit. $CBrClF_2$, needed for calibration (see below), was prepared by the bromination of $CHClF_2$. For this purpose a mixture of $CHClF_2$ (47 Torr) and Br_2 (1 Torr) was irradiated until GC analysis of the mixture showed the absence of Br_2 (under the experimental conditions the detection limit for Br_2 was found to be 0.075 Torr, indicating that at least 92.5% of Br_2 had reacted with $CHClF_2$).

Kinetic experiments were carried out in a greaseless static system, and the details of the experimental apparatus and procedure have been described elsewhere.[2] Reaction temperatures ranged from 80 to 150 °C and were maintained within 0.1 °C by circulating an ethylene glycol/water solution (approximately 4:1) through the outer jacket of the cylindrical Pyrex reactor. The irradiation time was varied from 2.5 to 30 min depending on the reaction temperature to keep the formation of the undesirable secondary bromination products as low as possible. Product analysis was carried out by isothermal gas chromatography (175 °C) with an electron capture detector (ecd) and a Durapak R column of 0.85-m length. Calibration curves of relative peak area vs pressure for the products $CBrClF_2$ and CH_2BrCl were determined by GC analyses of known amounts of these gases diluted with $CHClF_2$, yielding the linear relationships

$$S(CH_2BrCl) = (3177 \pm 50)P(CH_2BrCl) - (9.34 \pm 0.95) \times 10^4; \quad S = 1 \times 10^5 \text{ to } 5 \times 10^5$$

$$S(CBrClF_2) = (2354 \pm 28)P(CBrClF_2) - (1.31 \pm 0.08) \times 10^4; \quad S = 1 \times 10^4 \text{ to } 15 \times 10^4$$

where S denotes peak area (counts, range as indicated) and P the partial pressure of the compounds (mTorr). In the bromination experiments the observed peak area varied from 1×10^5 to 5×10^5 counts for CH_2BrCl and from 2.5×10^4 to 6.5×10^4 counts for $CBrClF_2$. Thus, the uncertainty of the product ratios arising from the calibration factors is evaluated to be 4.2–5.9%.

Preliminary experiments confirmed the absence of dark reactions: when a $CHClF_2/CH_3Cl/Br_2$ (100:20:6) mixture was kept in a shielded reactor for 30 min at 150 °C, no products were found. For the irradiated mixtures the observed carbon-containing products were $CBrClF_2$ and CH_2BrCl except for the experiments at 80.0 °C where trace amounts of $CHBr_2Cl$ (secondary bromination product of CH_3Cl) were also detected, owing to the long photolysis times required at this low temperature.

Results and Discussion

Kinetic Parameters. The kinetcs of gas-phase photobromination of $CHClF_2$ between 80 and 150 °C has been studied by the competitive method using CH_3Cl as an external reference and

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[†] Present address: Hitotsubashi University, Kunitachi, Tokyo, Japan.

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TABLE I: Experimental Conditions and Temperature Dependence of the Rate Constant Ratio k_1/k_2

T, °C	n^a	t^b	$P(CHClF_2)/P(CH_3Cl)^c$	$10^2(k_1/k_2)$
80.0	3	30	4.426	3.594 ± 0.013
85.6	6	18–20	4.491	3.736 ± 0.053
90.4	3		4.491	3.875 ± 0.053
96.0	3	14	4.491	4.149 ± 0.013
100.8	6	12	4.491	4.355 ± 0.082
105.6	6	10	5.083	4.425 ± 0.057
110.3	6	8	5.083	4.615 ± 0.097
115.2	3	6–7	4.491	4.856 ± 0.098
120.6	3	6	4.491	5.057 ± 0.022
125.9	3	5	4.425	5.209 ± 0.045
131.0	3	4–4.5	4.425	5.379 ± 0.051
140.5	3	3.5	4.425	5.743 ± 0.077
150.4	3	2.5–3	4.425	6.091 ± 0.160

[a] Number of runs. [b] Photolysis time (min). [c] Total partial pressure of halomethanes varied from 34.1 to 36.2 Torr, with $P(Br_2)$ fixed at 2.33 Torr.

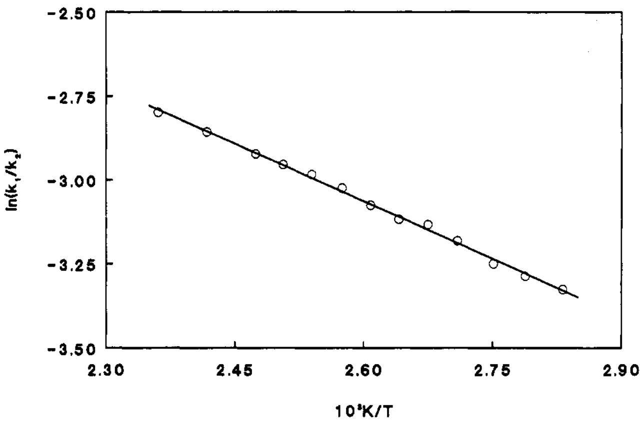

Figure 1. Temperature dependence of the rate constant ratio k_1/k_2 for hydrogen abstraction by bromine atoms from $CHClF_2$ and CH_3Cl as competitors.

related to C_2H_6, chosen as a primary reference compound. The general scheme for competitive bromination has been reviewed,[3] and the reactions of interest here are the rate-determining propagation steps:

$$CHClF_2 + Br \rightarrow CClF_2 + HBr \quad (1)$$

$$CH_3Cl + Br \rightarrow CH_2Cl + HBr \quad (2)$$

$$C_2H_6 + Br \rightarrow C_2H_5 + HBr \quad (3)$$

For sufficiently long chains and low conversion, <5%, with respect to competitors the reverse reactions may be neglected and the rate constant ratio is, without noticeable error, simply related to the measured product ratio

$$k_1/k_2 = [CBrClF_2][CH_3Cl]_0/[CH_2BrCl][CHClF_2]_0 \quad (4)$$

where the subscript 0 denotes the initial concentration. The validity of eq 4 was verified over a range of bromine pressures and photolysis times at a fixed competitor ratio. Thus, the relative rates, k_1/k_2, at 95.8 °C were independent of the irradiation time (11–22 min) and the initial bromine pressure (1.5–4.5 Torr) at a fixed total halomethane pressure of 36.5 Torr ($[CHClF_2]_0$ = 6.6 Torr, $[CH_3Cl]_0$ = 29.9 Torr).

The experimental conditions and temperature dependence of k_1/k_2 are listed in Table I and show that the product ratio $CBrClF_2/CH_2BrCl$ increases with temperature. Further, as shown in Figure 1 the rate constant ratios fit an Arrhenius rate law over the temperature range examined, and least-squares analysis of the plot yields the expression

$$\ln (k_1/k_2) = (-0.0885 \pm 0.0580) - (2274 \pm 40)/RT \quad (5)$$

TABLE II: Revised Activation Energies for Bromination of Methane and Halomethanes[a]

RH	R′H	$E_f(RH) - E_f(R'H)$	ref	$E_f(RH)^b$
CH_4	C_2H_6	4.92 ± 0.04	5	17.58 ± 0.36
CH_3F	CH_4	−2.48 ± 0.04	17	15.10 ± 0.36
CH_2F_2	CH_4	−2.00 ± 0.04	17	15.58 ± 0.36
CHF_3	CH_4	3.74 ± 0.08	5	21.32 ± 0.37
CH_3Cl	C_2H_6	1.06 ± 0.07	4	13.72 ± 0.36
CH_2Cl_2	CH_3Cl	−2.61 ± 0.32	*c*	11.10 ± 0.48
$CHCl_3$	CH_2Cl_2	−1.56 ± 0.18	*c*	9.54 ± 0.51
CH_2ClF	$CHCl_3$	5.49 ± 0.50	*c*	15.03 ± 0.71
$CHClF_2$	CH_3Cl	2.27 ± 0.04	*d*	15.99 ± 0.36
$CHCl_2F$	$CHCl_3$	4.03 ± 0.27	*c*	13.57 ± 0.58
CH_3Br	C_2H_6	2.65 ± 0.09	4	15.31 ± 0.37

[a] Activation energies in kilocalories per mole. [b] Based on C_2H_6 as primary reference compound (eq 8, see text). [c] Copp, D. E.; Tedder, J. M. *Int. J. Chem. Kinet.* **1972**, *4*, 69. [d] This work.

where R is in cal K^{-1} mol^{-1} and the stated uncertainties are 1 standard deviation.

Fettis et al.[4] have reported relative Arrhenius parameters for the competitive bromination of C_2H_6 and CH_3Cl in the temperature range 58–200 °C which overlaps that of the present study:

$$\ln (k_3/k_2) = (0.6403 \pm 0.0575) + (1055 \pm 68)/RT \quad (6)$$

Combining eqs 5 and 6 yields the rate constant ratio k_1/k_3 as

$$\ln (k_1/k_3) = (-0.7288 \pm 0.0817) - (3329 \pm 79)/RT \quad (7)$$

In our previous competitive bromination studies[2] we calculated absolute values of preexponential factors and activation energies based on the rate parameters for the bromination of ethane [$\log (A_3/(\mathrm{cm^3\ mol^{-1}\ s^{-1}})) = 14.14$; $E_3 = 13.66 \pm 0.14$ kcal mol^{-1}] reported by Amphlett and Whittle (AW),[5] which, in turn, are based on their direct thermal bromination of CF_3H and C_2F_5H by classical methods, and a series of cross-linked competitive studies.[5] Most recently, Davies et al.[6] determined k_3 directly over the temperature range 150–350 °C using laser flash photolysis of CF_2Br_2 as a source of Br atoms in the presence of C_2H_6, coupled with time-resolved detection of $Br(^2P_{3/2})$ by resonance fluorescence:

$$k_3/(\mathrm{cm^3\ mol^{-1}\ s^{-1}}) = (1.32 \pm 0.72) \times 10^{14} \exp[-(12658 \pm 358)/RT] \quad (8)$$

where R is in cal K^{-1} mol^{-1}. While the preexponential factor is almost identical to that reported by AW, the measured activation energy in this direct study is lower by 1.0 kcal mol^{-1}. The origin of this difference cannot be readily assessed. AW measured initial rates for Br + RH → R + HBr (R = CF_3, C_2F_5) by following the disappearance of Br_2 photometrically (which, according to AW, is difficult to measure accurately[5]), and combined these results with competitive measurements, which are much less susceptible to error. On the other hand, the direct kinetic spectroscopy results of Davies et al.[6] should be quite accurate for C_2H_6, where all C–H bonds are equivalent. For the purpose of evaluation of absolute rate parameters for reaction 1 and related thermochemical data (see below) we adopt here for k_3 the Arrhenius expression of Davies et al.[6], eq 8, with the tacit assumption that it is also valid at temperatures extending below 150 °C. Combination of eqs 7 and 8 gives

$$k_1/(\mathrm{cm^3\ mol^{-1}\ s^{-1}}) = (0.64 \pm 0.35) \times 10^{14} \exp[-(15987 \pm 367)/RT] \quad (9)$$

Table II summarizes revised activation energies for methane and some halomethanes derived from competitive studies (as indicated) recalculated using the new value of k_3 (eq 8) as the primary standard.

$\Delta H_f°(CClF_2)$ and $D°(CCl_2F\text{–}H)$. Kinetic and equilibrium studies of bromination reactions have been a major source of information on free radical heats of formation and bond dissociation energies. From kinetic data alone, thermochemical data are preferably determined from competition reactions including a well-known reference, since measurement of relative rate constants (and their T dependence) is inherently more accurate than their absolute determination.

For any pair of bromination reactions

$$\mathrm{RH} + \mathrm{Br} \rightleftharpoons \mathrm{R} + \mathrm{HBr} \qquad \Delta H^\circ(T_\mathrm{m})$$

$$\mathrm{R'H} + \mathrm{Br} \rightleftharpoons \mathrm{R'} + \mathrm{HBr} \qquad \Delta H^{\circ\prime}(T_\mathrm{m})$$

the difference in reaction enthalpies, $\Delta H^\circ - \Delta H^{\circ\prime}$ is given by

$$\begin{aligned}\Delta H^\circ(T_\mathrm{m}) - \Delta H^{\circ\prime}(T_\mathrm{m}) &= \Delta H_\mathrm{f}^\circ(\mathrm{R'H}) - \Delta H_\mathrm{f}^\circ(\mathrm{RH}) + \Delta H_\mathrm{f}^\circ(\mathrm{R}) - \Delta H_\mathrm{f}^\circ(\mathrm{R'}) \\ &= D^\circ(\mathrm{R{-}H}) - D^\circ(\mathrm{R'{-}H}) \\ &= (E_\mathrm{f} - E_\mathrm{f}') - (E_\mathrm{r} - E_\mathrm{r}')\end{aligned} \qquad (10)$$

where the last equation is written in terms of activation energies for the forward and reverse reactions and T_m denotes the mean temperature of the temperature range over which the activation energies are measured. The evaluation of heats of formation or bond dissociation energies at 298 K requires heat capacity data which is not available for the $\mathrm{CClF_2}$ radical. However, heat capacity corrections are usually quite small (e.g., for $\mathrm{CF_3}$, $\Delta H_\mathrm{f}^\circ{}_{298}$ values at 298 and 400 K differ by only 0.12 kcal mol^{-1}) and are neglected here.

Activation energies for the reverse reactions are difficult to measure but are known to be small. Traditionally, E_r values have been assumed[3,7] to be of the order of 2 ± 1 kcal mol^{-1} for any radical, R. Most recently, however, several researchers[8-13] and in particular Gutman and co-workers[8-11,13] reported directly measured rate constants for a series of free radical reactions with HBr and HI with the unexpected findings of small but *negative* temperature coefficients. For alkyl radicals the reported activation energies fall in the narrow ranges E_a = −0.31 to −1.39 kcal mol^{-1} for $\mathrm{R + HBr \rightarrow RH + Br}$[8-10] and E_a = −0.29 to −1.51 kcal mol^{-1} for $\mathrm{R + HI \rightarrow RH + I}$[11,12] where R = $\mathrm{CH_3}$, $\mathrm{C_2H_5}$, i-$\mathrm{C_3H_7}$, s-$\mathrm{C_4H_9}$, and t-$\mathrm{C_4H_9}$. The observed trend is that activation energies become more negative with increasing complexity of the alkyl radical. Activation energies for reaction of halogen-substituted methyl radicals with HI[13] show an interesting transition from small positive values (kcal mol^{-1}) for $\mathrm{CH_2Cl}$ (+0.26) and $\mathrm{CHCl_2}$ (+0.19) to small negative values for $\mathrm{CH_2Br}$ (−0.19) and $\mathrm{CH_2I}$ (−0.38). Gutman and co-workers[8-11] interpreted the negative activation energies in terms of a complex mechanism in which the radical is initially attracted to the halogen end of HX, followed by rotation of the hydrogen. However, this structural model is not supported by theoretical calculations for the $\mathrm{CH_3 + HBr \rightarrow CH_4 + Br}$ reaction[14] using the Gaussian-1 (G1) theory,[15] though theoretical evidence for the existence of a loosely bound complex along the reaction coordinate was obtained which does provide indirect support for a negative activation energy.[14]

Without pursuing further the question of negative activation energies, what is clear from the work of Gutman and co-workers, and earlier studies, is that the absolute magnitude of E_r is generally small; hence, the difference $|E_\mathrm{r} - E_\mathrm{r}'|$ in eq 10 will also be small. Therefore, it is not unreasonable, as a first approximation, to assign the value $E_\mathrm{r} - E_\mathrm{r}' \approx 0 \pm 1$ kcal mol^{-1} for compounds of a similar type. With this assumption eq 10 reduces to

$$D^\circ(\mathrm{R{-}H}) \approx D^\circ(\mathrm{R'{-}H}) + (E_\mathrm{f} - E_\mathrm{f}') - (0 \pm 1) \quad \mathrm{kcal\ mol^{-1}} \qquad (11)$$

For the evaluation of $D^\circ(\mathrm{CClF_2{-}H})$ and $\Delta H_\mathrm{f}^\circ(\mathrm{CClF_2})$ we choose $\mathrm{CHF_3}$ and $\mathrm{CHCl_3}$, respectively, as suitable reference compounds. The choice of two independent references provides a cross-check. The C–H bond dissociation energy in $\mathrm{CHF_3}$ is generally accepted on the basis of exhaustive studies by Whittle and co-workers.[5,16-20] The latest recommended value is $D^\circ(\mathrm{CF_3{-}H})$ = 106.3 ± 0.5 kcal mol^{-1}.[20] From Table II, $E_\mathrm{f}(\mathrm{CHClF_2})$ = 15.99 ± 0.36 kcal mol^{-1} and $E_\mathrm{f}(\mathrm{CHF_3})$ = 21.32 ± 0.37 kcal mol^{-1}; hence, from eq 11 $D^\circ(\mathrm{CClF_2{-}H})$ = 101.0 ± 1.2 kcal mol^{-1}. With $\Delta H_\mathrm{f}^\circ{}_{298}(\mathrm{CHClF_2})$ = −115.3 ± 0.8 kcal mol^{-1},[21] this leads to $\Delta H_\mathrm{f}^\circ{}_{298}(\mathrm{CClF_2})$ = −66.4 ± 1.4 kcal mol^{-1}.

Most recently, Hudgens et al.[22] have redetermined $\Delta H_\mathrm{f}^\circ{}_{298}(\mathrm{CCl_3})$ = 17.0 ± 0.6 kcal mol^{-1} based on kinetic spectroscopy measurements. This value supersedes previous compilations (19 ± 1 kcal mol^{-1}).[7] With the revised value of $\Delta H_\mathrm{f}^\circ(\mathrm{CCl_3})$ and $\Delta H_\mathrm{f}^\circ{}_{298}(\mathrm{CHCl_3})$ = −24.76 ± 0.3 kcal mol^{-1},[21] one calculates $D^\circ(\mathrm{CCl_3{-}H})$ = 93.9 ± 0.7 kcal mol^{-1}. From Table II, $E_\mathrm{f}(\mathrm{CHCl_3})$ = 9.54 ± 0.51 kcal mol^{-1}, and using eq 11, one obtains $D^\circ(\mathrm{CClF_2{-}H})$ = 100.4 ± 1.4 kcal mol^{-1} and hence $\Delta H_\mathrm{f}^\circ{}_{298}(\mathrm{CClF_2})$ = −67.0 ± 1.6 kcal mol^{-1}. The bromination results based on two independent reference reactions are in good agreement. The largest uncertainty derives from the assumption that $\Delta E_\mathrm{r} = E_\mathrm{r} - E_\mathrm{r}' \approx 0 \pm 1$ kcal mol^{-1}. A more conservative though perhaps unwarranted assignment of $\Delta E_\mathrm{r} = 0 \pm 2$ kcal mol^{-1} would raise the uncertainties in $D^\circ(\mathrm{CClF_2{-}H})$ and $\Delta H_\mathrm{f}^\circ(\mathrm{CClF_2})$ by ca. 0.9 kcal mol^{-1}. These values may be compared with earlier determinations in the literature. Kaufman and Reed[23] deduced an approximate value, $\Delta H_\mathrm{f}^\circ(\mathrm{CClF_2})$ = −69 ± 4 kcal mol^{-1}, from the reaction of $\mathrm{CF_2Cl_2}$ with sodium vapor by the diffusion flame method. Foon and Tait[24] obtained $\Delta H_\mathrm{f}^\circ{}_{298}(\mathrm{CClF_2})$ = −67.9 ± 4 kcal mol^{-1} from relative rate measurements of the fluorination of $\mathrm{CCl_2F_2}$. This value is subject to assumed activation energies for the reverse of the process $\mathrm{F + RCl \rightarrow ClF + R}$ of several chlorofluorocarbons considered. Leyland et al.[25] measured absolute Arrhenius parameters for the reaction $\mathrm{CF_3 + CHClF_2 \rightleftharpoons CF_3H + CClF_2}$ and its reverse in static photolysis experiments. Hexafluoroacetone was used as a source of $\mathrm{CF_3}$ radicals in the presence of $\mathrm{CHClF_2}$ for the forward reaction, while conversely, 1,2-dichlorotetrafluoroacetone was a source of $\mathrm{CClF_2}$ radicals in the presence of $\mathrm{CHF_3}$. From the difference in the energies of activation and the then available thermochemical data, Leyland et al. derived $D^\circ(\mathrm{CClF_2{-}H})$ = 103.8 ± 1 kcal mol^{-1} and $\Delta H_\mathrm{f}^\circ(\mathrm{CClF_2})$ = −64.3 ± 2 kcal mol^{-1}. Recalculation using thermochemical data from the most recent compilation[21] leads to slightly revised values: $D^\circ(\mathrm{CClF_2{-}H})$ = 103.4 ± 1 and $\Delta H_\mathrm{f}^\circ(\mathrm{CClF_2})$ = −64.0 ± 1.2 kcal mol^{-1}. In their review of bond energies and radical heats of formation, McMillen and Golden[7] list the value of Leyland et al. for $\Delta H_\mathrm{f}^\circ{}_{298}(\mathrm{CClF_2})$ but also give $D(\mathrm{CClF_2{-}H})$ = 101.6 ± 1.0 kcal mol^{-1} (quoting the unpublished work of E. Whittle); however, these numbers are not compatible with $\Delta H_\mathrm{f}^\circ(\mathrm{CHClF_2})$ = −115.3 ± 0.8 kcal mol^{-1} recommended by Pedley et al.[21] We consider the evaluated heat of formation and bond dissociation energy based on our bromination results and two independent reference reactions to be more reliable, the mean values being $D^\circ(\mathrm{CClF_2{-}H})$ = 100.7 kcal mol^{-1} and $\Delta H_\mathrm{f}^\circ{}_{298}(\mathrm{CClF_2})$ = −66.7 kcal mol^{-1} with a conservative estimate of the uncertainties of ±2 kcal mol^{-1}, making allowance for the neglect of heat capacity corrections. Finally it may be noted that our value of $\Delta H_\mathrm{f}^\circ(\mathrm{CClF_2})$ is remarkably close to −66 kcal mol^{-1} estimated by Lias et al.[26] based on the observation that the reaction $\mathrm{C_2H_5^+ + CCl_2F_2 \rightarrow CClF_2^+ + C_2H_5Cl}$ is nearly thermoneutral, and a theoretical value of −65.2 ± 2.8 kcal mol^{-1} based on a consideration of iso/homodesmic reactions.[27]

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Registry No. **1**, 75-45-6; **2**, 74-87-3; $\mathrm{CH_4}$, 74-82-8; $\mathrm{CH_3F}$, 593-53-3; $\mathrm{CH_2F_2}$, 75-10-5; $\mathrm{CHF_3}$, 75-46-7; $\mathrm{CH_2Cl_2}$, 75-09-2; $\mathrm{CHCl_3}$, 67-66-3; $\mathrm{CH_2ClF}$, 593-70-4; $\mathrm{CHCl_2F}$, 75-43-4; $\mathrm{CH_3Br}$, 74-83-9; $\mathrm{CClF_2}$, 1691-89-0; Br, 10097-32-2.

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Surface-Induced Stirring Effects in the Mn-Catalyzed Belousov–Zhabotinskii Reaction with a Mixed Hypophosphite/Acetone Substrate in a Batch Reactor

John A. Pojman,* Herbert Dedeaux, and Dionne Fortenberry

Department of Chemistry and Biochemistry, University of Southern Mississippi, Hattiesburg, Mississippi 39406-5043 *(Received: January 6, 1992; In Final Form: June 2, 1992)*

A manganese-catalyzed Belousov–Zhabotinskii (BZ) reaction with a mixed hypophosphite/acetone substrate was found to be remarkably sensitive to stirring in a batch reactor. The reaction oscillated in a container with a gas/liquid interface (either air or nitrogen). However, when the reaction was stirred in a sealed flask with no interface, the system remained in the reduced state. When the slow stirring (about 100 rpm) was stopped, a pink color from Mn(III) was observed to ascend from the Teflon-coated stir bar. When a glass stir bar was used, the system would oxidize much more slowly than with the Teflon one. A possible mechanism is considered in which bromine loss to the gas phase is crucial for oscillation. In the sealed system, oxidation occurs when the stirring is stopped because bromine can adsorb to the surface of the Teflon, allowing local oxidation which spreads throughout the system.

Oscillating reactions are known to be sensitive to the rate of stirring.[1-7] In continuous-stirred tank reactors (CSTRs) the stirring effects can occur because of imperfect mixing of the feedstreams.[8] However, in batch reactors two mechanisms have been proposed.

The first mechanism involves the transfer of gases into and from the solution. Batch reactions of the Belousov–Zhabotinskii (BZ) reaction are sensitive to oxygen, and the rate of stirring affects the amount of O_2 entrained into the system.[1,9,10] However, Sevčík and Adamciková found stirring effects even with an inert atmosphere.[11,12]

Batch BZ reactions are sensitive to the transfer of bromine out of the system. Noszticzius and Bodiss demonstrated that a BZ system with an oxalic acid substrate (which cannot react with bromine) can oscillate if a stream of inert gas is bubbled through the solution and that the oscillating period and amplitude depend on the rate of gas flow.[13,14] The system would oscillate without a gas stream if acetone was present as a bromine removal agent.[15]

López-Tomás and Sagués observed sensitivity to the rate of stirring in the cerium/malonic acid BZ system when using a nitrogen atmosphere, which they attributed to the stirring affecting the rate of bromine loss.[2] Noszticzius et al.[3] reported stirring effects in both the batch and CSTR for the cerium/oxalic acid/acetone BZ system in a poly(methyl methacrylate) reactor. The system would not start oscillating unless stirring was stopped. They proposed that bromine could be adsorbed by the reactor walls in the absence of stirring. The autocatalytic bromous acid production[10] (and oxidation of the metal ion catalyst) could start in the surface layer and then spread throughout the bulk when stirring was resumed.

Noszticzius et al.[4] recently proposed that the rate of recombination reactions between very low concentration radicals could be affected by the rate of stirring (varying between 300 and 2000 rpm) in a batch reactor due to hydrodynamic turbulence. They proposed this mechanism for the stirring effects in batch reactions of the BZ reaction (cerium catalyst with malonic acid substrate).

We have observed interesting stirring effects with a modified version of the Belousov–Zhabotinskii reaction developed by Ouyang et al. in which the catalyst is manganese with a mixed substrate of hypophosphite and acetone.[16] This system is noteworthy because of its lack of bubble formation.

In this system, spontaneous oscillations would not occur unless a gas/liquid interface was present during stirring. If no such interface was present, then the system remained in a reduced state until stirring was stopped, at which time a wave of oxidation could be observed to spread from the Teflon-coated stir bar. Our observations support the mass transfer of bromine mechanism and not the radical recombination mechanism in this case.

Experimental Section

All chemicals, namely, acetone (Baker), $MnSO_4 \cdot H_2O$ (Baker), NaH_2PO_2 (Sigma), concentrated H_2SO_4 (Fisher), and $NaBrO_3$ (Aldrich), were of reagent grade and used without further purification. The reaction solution was made with the following composition from reagent grade chemicals: acetone (0.33 M), H_2SO_4 (2.0 M), NaH_2PO_2 (0.022 M), $NaBrO_3$ (0.0095 M), $MnSO_4$ (0.0095 M). Stirring was accomplished with a magnetic stirrer. All reactions were performed at ambient temperature (23 °C).

The effect of a gas/liquid interface was determined by running the reaction in two different reactors. One reactor consisted of a 250-mL round bottom flask with a glass stopper and no gas/liquid interface. The platinum electrode (Rainin) and Hg/$HgSO_4$ reference electrode (Rainin) were sealed into the sides of the flask.

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