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QUENCHING OF UF_6 (A STATE) BY HALOMETHANES

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Summary

UF_6 (A state) was produced by laser irradiation of UF_6 at 393.5 nm. Rate constants at room temperature have been determined for the removal of UF_6 (A state) by various halomethanes. The following rate constants (units of 10^{11} l mol^{-1} s^{-1}) were determined: CF_4, 0.016; CCl_4, 3.4; $CFCl_3$, 2.0; CF_2Cl_2, 0.64; CF_3Cl, 0.088; $CFCl_2H$, 2.6; CF_2ClH, 0.69; CF_2Br_2, 3.2; CF_3Br, 2.5. The observed quenching rate constants appear to be consistent with a mechanism that involves an inversion of the halomethane configuration, ejection of a bromine or chlorine atom and the formation of UF_5 and the new halomethane.

1. Introduction

There has been considerable interest recently in the dynamics of UF_6 (A state), hereafter denoted $^*UF_6$ [1 - 10]. Much of the work has been concerned with investigating UF_6 self-quenching [1 - 5, 8] while only limited attention has been focused on the dynamics of $^*UF_6$ in the presence of foreign gases [6, 7, 9, 10]. We have noted in earlier work that $^*UF_6$ is quenched inefficiently by various inorganic gases such as He, Ar, H_2, CO, F_2, N_2 and SF_6 [9]. The quenching studies involving selected alkanes have given some rather surprising results. Nearly all the alkanes investigated, such as C_2H_6, C_3H_8 and n-C_4H_{10} [10], exhibited very large $^*UF_6$ quenching rate constants. The lone exception was CH_4, which was almost two orders of magnitude less efficient than all the other alkanes. The energy levels of the alkanes are sufficiently higher than that of $^*UF_6$ so that no favorable physical energy transfer mechanism exists. Therefore the work with the alkanes indicated that the dominant quenching route must be chemical in nature. We have undertaken the present investigation to determine whether chloro-substituted or bromo-substituted methanes are significantly different from CH_4 in their ability to quench $^*UF_6$. It was hoped that this might help elucidate the disparity in rate constants between CH_4 and the other alkanes.

2. Experimental

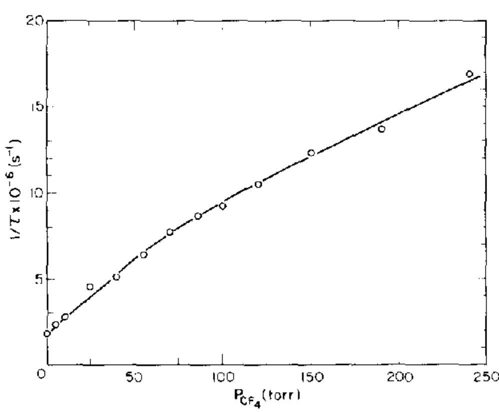
The emission cell is machined out of an aluminum block and is fitted with Suprasil II windows. The cell is connected to a gas circulation system consisting of a Metal Bellows Corporation pump and two large ballast tanks. The pumps ensure proper mixing of reactants and the ballast tanks minimize any depletion of UF_6 in an experiment. The system is primarily constructed of aluminum, Monel and nickel. Pressures are measured with various MKS Baratron capacitance manometers. All experiments were conducted at room temperature (23 - 27 °C).

The UF_6 is excited with a Molectron N_2-pumped dye laser that has pulses of spectral width 0.14 Å and duration 5 ns. The lasing wavelength is determined by a Spex 1 m monochromator. The fluorescence is viewed perpendicular to the laser beam through a 422.5 nm dielectric filter and is focused onto an RCA 7265 photomultiplier tube. The signal from the photomultiplier is properly processed and is sent to a Tektronix 7844 oscilloscope where about 20 - 80 shots of the displayed decay are photographically superimposed and the lifetime of the decay is subsequently evaluated.

UF_6 was supplied in-house and was properly handled to render it free of contaminants. All other chemicals were obtained commercially and were used without further purification.

3. Results

Figure 1 depicts the Stern–Volmer plot for quenching of $^*UF_6$ by CF_4. The pressure of UF_6 was 3.00 Torr for Fig. 1 and also for all other Stern–Volmer plots. The curvature noted in Fig. 1 is similar to those of the Stern–



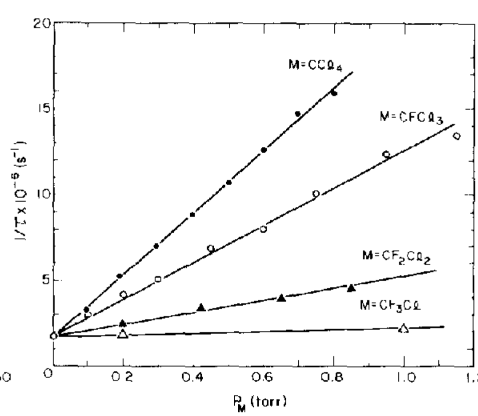
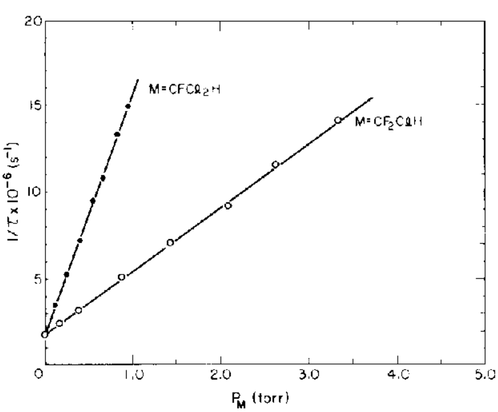


Fig. 1. Stern–Volmer plot for CF_4: $P(UF_6)$, 3.00 Torr; excitation wavelength, 393.5 nm.

Fig. 2. Stern–Volmer plots for CCl_4 (closed circles), $CFCl_3$ (open circles), CF_2Cl_2 (closed triangles) and CF_3Cl (open triangles): $P(UF_6)$, 3.00 Torr; excitation wavelength, 393.5 nm.

Volmer plots previously obtained for other quenchers [9] which remove $^*UF_6$ via both chemical and physical quenching channels. Figure 2 displays Stern–Volmer plots for CCl_4, $CFCl_3$, CF_2Cl_2 and CF_3Cl. All the data points for CF_2Cl_2 and CF_3Cl are not shown; however, all data points were used in evaluating their slopes. The rate constants derived from these slopes are indicative of very efficient quenching processes which continually increase in magnitude as the fluorine atoms are sequentially replaced by chlorine atoms. Figure 3 graphically presents our quenching results for $CFCl_2H$ and CF_2ClH and again we can note that the slope is significantly greater when more chlorine atoms are present. Figure 4 illustrates that additional bromine substitution increases the quenching as evidenced by the slope for the CF_2Br_2 Stern–Volmer plot being larger than that for CF_3Br. Table 1 presents all the rate constants determined in this study.



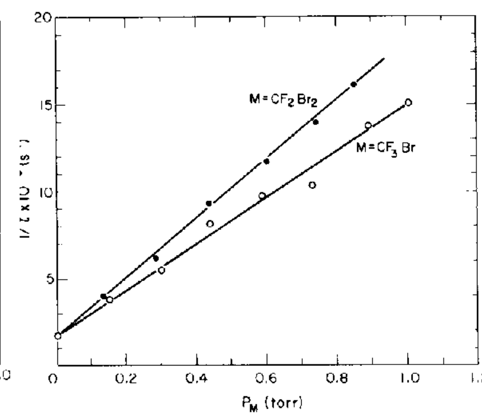


Fig. 3. Stern–Volmer plots for $CFCl_2H$ (closed circles) and CF_2ClH (open circles): $P(UF_6)$, 3.00 Torr; excitation wavelength, 393.5 nm.

Fig. 4. Stern–Volmer plots for CF_2Br_2 (closed circles) and CF_3Br (open circles): $P(UF_6)$, 3.00 Torr; excitation wavelength, 393.5 nm.

4. Discussion

The magnitude of the quenching rate constants for removal of $^*UF_6$ by the halomethanes varies in the range $(0.016 - 3.4) \times 10^{11}$ l mol^{-1} s^{-1} in going from CF_4 to CCl_4. The small rate constant for quenching by CF_4 can be attributed to the absence of any efficient physical energy transfer channel and also to the chemical inertness of the C–F bond which severely restricts chemical quenching. There are no electronic states for any of the halomethane quenchers which lie lower than the electronic energy available in $^*UF_6$ after excitation by 393.5 nm radiation. The absence of any exothermic electronic–electronic transfer channel excludes physical quenching proceeding at a rapid rate for any of the quenchers under consideration. Thus, there

TABLE 1

Rate constants k at room temperature for quenching of $^*UF_6$ by selected halomethanes M [a]

M	k (10^{11} l mol^{-1} s^{-1})
CF_4	0.016 [b]
CCl_4	3.4
$CFCl_3$	2.0
CF_2Cl_2	0.64
CF_3Cl	0.088
$CFCl_2H$	2.6
CF_2ClH	0.69
CF_2Br_2	3.2
CF_3Br	2.5

[a] The excitation wavelength was 393.5 nm and $P(UF_6)$ was 3.00 Torr for all experiments.
[b] Rate constant derived from the low pressure slope.

must be some efficient chemical quenching channel available for $^*UF_6$ + CCl_4 and other halomethanes which have quenching rate constants consistent with very efficient removal of $^*UF_6$. Also, the rate constant for quenching of $^*UF_6$ by CH_4 has been found to be 0.061×10^{11} l mol^{-1} s^{-1} [10] and it seems evident that chemical channels are available for the halomethanes that are not nearly as attractive when CH_4 is the quencher.

Our earlier work had shown that the quenching reactions of $^*UF_6$ by alkanes could be rationalized on the basis of a reaction involving the simultaneous removal of two hydrogen atoms from the alkanes. The analogous reaction for CCl_4 would be

$$^*UF_6 + CCl_4 \rightarrow UF_4 + CCl_2 + 2FCl \quad (1)$$

Reaction (1) is 115.7 kcal mol^{-1} endothermic [11, 12] and consequently is not a very plausible candidate to explain the very large quenching rate constant that we observe. Let us consider other thermochemically more favorable routes.

Two reactions that may serve as possible chemical routes to explain the very large rate constant for $^*UF_6$ + CCl_4 are

$$^*UF_6 + CCl_4 \rightarrow CCl_3F + Cl + UF_5 \quad (2)$$

$$^*UF_6 + CCl_4 \rightarrow CCl_3 + ClF + UF_5 \quad (3)$$

A consideration of available thermochemical data for these species [11, 12] indicates that reaction (2) will be exothermic by 40.6 kcal mol^{-1} and reaction (3) will be endothermic by 6.3 kcal mol^{-1}. Thus, on the basis of thermodynamics reaction (2) looks like the more probable reaction channel.

With regard to the two possible types of reaction under consideration let us consider the reaction of $^*UF_6$ + CF_3Br which also has a very large quenching rate constant:

$$*UF_6 + CF_3Br \rightarrow CF_4 + Br + UF_5 \quad (4)$$

$$*UF_6 + CF_3Br \rightarrow CF_3 + BrF + UF_5 \quad (5)$$

Reaction (4) is calculated to be exothermic by 64.7 kcal mol^{-1} and reaction (5) is endothermic by 5.2 kcal mol^{-1} [11, 12]. On the basis of thermodynamics reaction (4) would certainly be favored over reaction (5). While thermodynamics cannot always predict correctly which reaction pathway will be kinetically favored, it serves as a very useful guide in the absence of other more detailed information. Since the $*UF_6$ dissociates into UF_5 and fluorine atoms [13] and the fluorine atom can undergo significant secondary reactions with the quenchers present in this study, product analysis cannot provide unambiguous information regarding which kinetic route is dominant. However, it does seem likely that reaction (5) is unimportant relative to reaction (4).

Enough information is available in the literature so that thermochemical calculations can be carried out for other halomethane reactions of the type illustrated by reactions (2) and (4) above. There is not enough information to perform the necessary calculations for reactions similar to reactions (3) and (5) owing to the absence of reliable information on the heats of formation of the various halogenated methyl radicals, but this reaction pathway does not seem to be thermochemically favorable as noted above. All of the reactions of the type (2) and (4) are found to be exothermic by a minimum of 40.7 kcal mol^{-1}. The exothermicity of this type of atom displacement reaction is quite consistent with the large quenching rate constants.

With the assumption that reactions (2) and (4) represent the overall quenching chemistry, the following molecular dynamic scheme seems plausible. The $*UF_6$ probably approaches the halomethane opposite the halogen–carbon bond that is eventually broken. A fluorine atom of the $*UF_6$ could then bond to the carbon atom, causing an inversion of the halomethane configuration and the expulsion of the halogen atom. In contrast, the mechanism suggested by reactions (3) and (5) would have implied that the $*UF_6$ interact more directly with the halogen atom being abstracted from the halomethane.

The relative rate constants for the various halomethanes appear to be consistent with this dynamic scheme. For example, as we progress through the series CF_3Cl, CF_2Cl_2, $CFCl_3$ and CCl_4, the increase in rate constant is probably due to the $*UF_6$ having a higher probability of colliding opposite a chlorine atom on the substituted methane because of their increased number. This same explanation seems reasonable for the differences noted for $CFCl_2H$ and CF_2ClH and for CF_3Br and CF_2Br_2. The larger quenching efficiency by the bromomethanes over the chloromethanes may be related to the differences in the strengths of the carbon–halogen bond being broken. A comparison of the quenching rate constants for CF_2ClH and CF_3Cl, 0.69×10^{11} and 0.088×10^{11} l mol^{-1} s^{-1} respectively, reveals a dramatic difference in quenching efficiency. The decreased efficiency of the CF_3Cl may be due to steric hindrance and electrostatic repulsion of the additional fluorine atom with the in-coming $^*UF_6$.

In conclusion, the chloromethanes and bromomethanes have the ability to quench $^*UF_6$ much more efficiently than CH_4. The chloromethanes and bromomethanes have a very favorable thermochemical route available to them which appears to involve an inversion of the halomethane configuration, ejection of the bromine or chlorine atom and the formation of UF_5 and the new halomethane. This mechanism may represent an alternative explanation for the disparity between the quenching rate constants of CH_4 and the other alkanes which we reported earlier. However, at this time there is not sufficient information to make a judicious choice between the possible mechanistic routes.

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