Unimolecular Decomposition of F_2SO_3-Calculation by Reduced Kassel Integral in Factorized Form

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The unimolecular decomposition of fluorine fluorosulfonate at 374.2; 384.2 and 394.2 K, is calculated by means of the Reduced Kassel Integral in Factorized Form, an important method developed by J. Troe. The results are compared with those obtained by the RRKM method and experimental work.

Introduction

In order to calculate the falloff curves for thermal unimolecular reactions several considerations must be taken into account.

In the intermediate falloff range between low and high pressure limits, problems with energy transfer, activated complex location, lifetime distributions, centrifugal effects, etc., enter the rate constant. A full calculation of the rate constant, therefore, is extremely difficult and has in fact never been done. Thus, to believe in the results of the nowavailable RRKM falloff programs appears unrealistic because they do not take into account all these factors.

J. Troe has developed a method for the calculation of reduced falloff curves for strong collisions, from simple Kassel Integrals, where the Kassel parameters a and b have been replaced by the effective values S_k and B_k, fixed by the properties of the limiting rate constants k_0 and k_∞ [1, 2].

The Reduced Kassel Integrals with S_k and B_k fit most effectively the behaviour of reduced falloff curves. Nevertheless, RRKM calculations suggest that these curves are slightly too broad.

Therefore, J. Troe derived simple analytical expressions which correct this defect, by using the Reduced Kassel Integrals as a guideline to the functional form of the falloff expressions and by scaling it according to numerical RRKM calculations for a variety of molecules [3].

In order to do that, J. Troe represents reduced curves in factorized form.

The simplest transition curve is given by the Lindemann-Hinshelwood expression $F^{\mathrm{LH}}(k_0/k_\infty)$, which corresponds to a constant energy independent specific rate constant $k(E)$.

The broadening of the reduced falloff curves because of the energy dependence of $k(E)$ is then accounted for by a strong collision broadening factor $F^{\mathrm{SC}}(k_0/k_\infty)$. Weak collision effects introduce a further broadening described by a weak collision broadening factor $F^{\mathrm{WC}}(k_0/k_\infty)$.

Thus

$$k/k_\infty = F^{\mathrm{LH}}(k_0/k_\infty)\,F^{\mathrm{SC}}(k_0/k_\infty)\,F^{\mathrm{WC}}(k_0/k_\infty)\,,$$

where each factor would be calculated as in [3].

The above simple approximate technique is an important development. As such, it needs to be widely tested against experimental data and the RRKM theory. The present paper gives an example.

Several unimolecular decompositions were investigated by Czarnowski and Schumacher. They studied the fluorine fluorosulfonate decomposition in the presence of SO_3 at 374.2; 384.2 and 394.2 K. The rate determining step is the unimolecular process [4]

$$F_2SO_3 \rightarrow FSO_3 + F$$

with

$$k_\infty = 1.23 \times 10^{15} \exp(-33.0/R\,T)\ \mathrm{sec}^{-1}\,.$$

The unimolecular decomposition of this compound was calculated by the RRKM method [5].

Results and Discussion

The falloff curves were calculated at 374.2; 384.2 and 394.2 K up to 200 torr by means of the Reduced Kassel Integral in Factorized Form.

The Kassel parameter S_k was calculated as in reference [3], by means of the frequencies of the molecule [6], using the approximation $S_k = S_{\mathrm{eff}} + 1$, where S_{eff} is applied to those internal coordinates which contribute to the overcoming of the threshold energy, these coordinates in general being oscillators and internal rotors.

At first, the OF group of the F_2SO_3 molecule may be considered as an active internal rotor. However, previous results [7] established that a hindrance of

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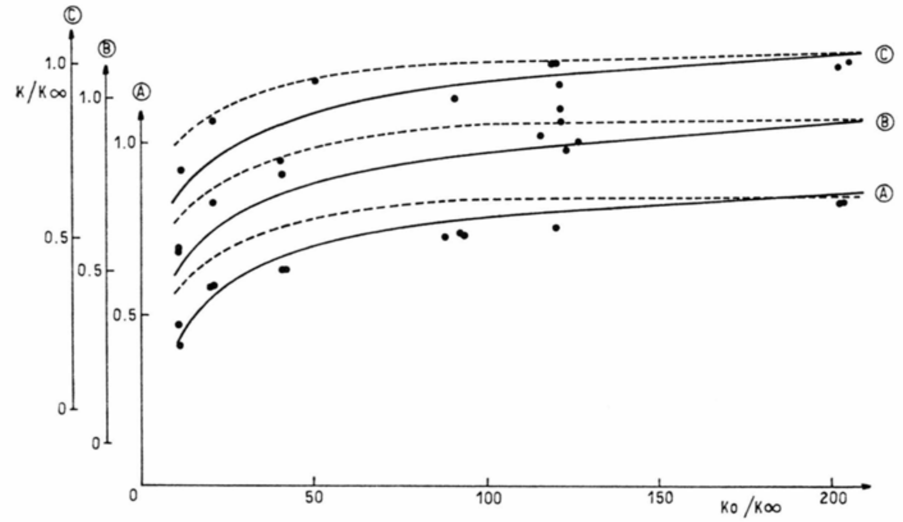

Fig. 1. Comparison of the calculated falloff curves with experimental results ●; – – – – Reduced Kassel Integral in Factorized Form; ——— RRKM.

free rotation around the SO bond in the FSO group must be assumed, presumably caused by some weaker pπ → dπ bonding.

Considering the molecular geometry and the torsional frequency of 137 cm^{-1}, a value of nearly 8 kcal mol^{-1} can be estimated for the barrier of torsional motion, and as the thermal energy is only 0.8 kcal mol^{-1}, internal rotation was not considered in the calculation.

The experimental efficiency factor for SO_3 relating to F_2SO_3 is 0.7 [4]. This factor was considered to be the same as the weak collision efficiency factor β_c.

The input data are given in Table 1, where the Kassel parameters S_k and B_k were calculated as in reference [3]. The calculated falloff curves, together with those obtained by the RRKM method [5] and the experimental results are shown in Figure 1.

Table 1. Input data for the calculated falloff curves.

	S_k	B_k	E_0	β_c
374.2 K	4.6	18.5	32.3	0.7
384.2 K	4.7	18.5	32.2	0.7
394.2 K	4.8	18.4	32.2	0.7

A satisfactory agreement was obtained between the calculated values by the Reduced Kassel Integral in Factorized Form and the experimental results. Furthermore, the quality of the reduced falloff curves compared to the RRKM calculations is seen to be excellent.

The advantage of these evaluations is that they can be done quickly and without the use of a computer. The application of this method only requires the knowledge of molecular properties. Thus, conjectures about an activated complex or a reaction coordinate are avoided.

The transition between the low pressure and high pressure limit, $p_{1/2}$, at different temperatures, could be calculated. The values of 9.5; 9.9 and 10.8 torr for 374.5; 384.5 and 394.5 K, respectively, were obtained according to the experimental values of $p_{1/2}(374.2\ \mathrm{K}) = 10.9 \pm 0.5$; $p_{1/2}(384.2\ \mathrm{K}) = 11.4 \pm 0.5$ and $p_{1/2}(394.5\ \mathrm{K}) = 13.0 \pm 1.9$ torr.

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