Chemical Communications

NUMBER 8/1967 26 APRIL

The Kinetics of the Decomposition of Chemically Activated Ethyl Fluoride

By J. A. Kerr, A. W. Kirk, B. V. O'Grady, and A. F. Trotman-Dickenson
(Edward Davies Chemical Laboratory, Aberystwyth)

The degree of activation of a molecule by chemical processes can be controlled by variations in the reaction systems. Thus methylcyclopropane can be made from methylene and cyclopropane with a higher energy than from propene; further variations can be achieved by changes in the source of methylene.[1] The range of energies is then fairly narrow. It is, however, possible to make activated ethyl fluoride with three widely different energy contents.

The formation and decomposition of chemically activated ethyl fluoride was first reported some six years ago.[2] Further work by us has shown that the observed decomposition was largely caused by self-heating of the reaction mixture. Nevertheless at much lower pressures than were first used, ethyl fluoride formed by reaction (1) as a step in the reaction between ethane and fluorine

$$C_2H_5 + F_2 = C_2H_5F^* + F \qquad (1)$$

does decompose by loss of hydrogen fluoride. The rate of this reaction can be found by comparison with the rate of deactivation of the fluoride k_d,

$$C_2H_5F^* = C_2H_4 + HF \qquad (k_e)$$

$$C_2H_5F^* + M = C_2H_5F + M \qquad (k_d)$$

The experiments were carried out in Pyrex vessels at room temperature as previously.[2] Reaction occurred rapidly on mixing. The products were analysed for ethylene and ethyl fluoride and an excellent plot of the function

$$[C_2H_4]/[C_2H_5F] = (k_e/k_d)(1/[M])$$

was obtained between 0·08 and 2·0 torr. Hence k_e can be calculated from k_e/k_d on the assumption that log k_d(torr^{-1} sec.$^{-1}$) is equal to the collision frequency 7·0. This appears to be the first observation of the chemical activation of a polyatomic molecule by a bimolecular reaction in which two molecules of product are formed. From the strength of the C–F (106 kcal.mole^{-1}) and F–F bonds (37 kcal.mole^{-1}),[3] the heat of reaction (1) is 69 kcal.mole^{-1}. Some of this energy can be dissipated as relative kinetic energy of the products, but qualitative consideration of the relative strengths of the bonds indicates that most of the energy will remain with the ethyl fluoride.

Activated ethyl fluoride can also be formed by the combination of methyl and fluoromethyl radicals (2)

$$CH_3 + CH_2F = C_2H_5F^{**} \qquad (2)$$

Experiments have been carried out at 40° in a quartz vessel. Analysis was again for ethyl fluoride and ethylene and a relation was found between 10 and 120 torr that yielded k_e/k_d. The energy content of the molecules can be taken

TABLE

Source	Energy Content E (kcal.mole^{-1})	log k_e (obs) (sec.$^{-1}$)	log k_e (calc.) (sec.$^{-1}$)
Reaction 1 (Abstraction)	69	6·78	6·79
Reaction 2 (Combination)	85·4	9·0	8·96
Reaction 3 (Insertion)	115	10·46	10·57

[log k_e (calc) given for assumed activation energy of 51 kcal.mole^{-1}.]

as 85 kcal.mole^{-1}, the quantity recommended by Benson and Haugen[4] for a similar reaction.

Ethyl fluoride of still higher energy content was made by the photolysis of keten with methyl fluoride (3) in the presence of large amounts of oxygen in a Pyrex vessel with the full light of a

$$CH_2 + CH_3F = C_2H_5F^{***} \qquad (3)$$

medium-pressure mercury arc between 220 and 3800 torr. Neopentane was added to provide a standard measure of the amount of ethyl fluoride initially formed; ethylene was formed from methylene reacting with keten so was not suitable as a measure of the decomposition. Products were analysed for ethyl fluoride and 2,2-dimethylbutane. All ethyl fluoride is formed by the insertion of singlet methylene. By comparison with other systems[5] the energy content of the fluoride is 115 kcal.mole^{-1}.

A proper treatment of the results in the Table depends upon a knowledge of the activation energy, E_0, of the thermal reaction. This could not be determined in static or flow systems because the runs were irreproducible. The correlation that can be achieved using the simple Kassel equation is of interest. The A factor can be taken as $10^{13\cdot5}$ sec.$^{-1}$ as for other elimination reactions of alkyl halides.[6] The number of oscillators can be taken as 12·5 from comparison with the cyclopropanes[7] C_3H_6, 13; C_3H_5F, 15; $C_3H_4F_2$, 17. The best fit in

$$\log k_e = 13\cdot5 + 11\cdot5 \log (1 - E_0/E)$$

is given when E_0 is 51 kcal.mole which leads to the values of k_e (calc) as shown. Thus E_0 is markedly lower than that estimated by Benson and Haugen.[7] Further work in this laboratory supports low values of activation energies for fluoride decompositions, but the use of a non-quantised model for unimolecular reaction tends to lead to an underestimate of activation energies.

(*Received, December 12th*, 1966; *Com.* 982.)

---

[1] J. N. Butler and G. B. Kistiakowsky, *J. Amer. Chem. Soc.*, 1960, **82**, 759.
[2] G. C. Fettis and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1960, 1064.
[3] J. A. Kerr, and A. F. Trotman-Dickenson, "Handbook of Chemistry and Physics," 47th Edn., Chemical Rubber Co., Cleveland, 1966.
[4] S. W. Benson and G. R. Haugen, *J. Phys. Chem.*, 1965, **69**, 3898.
[5] D. W. Setser and B. S. Rabinovitch, *Canad. J. Chem.*, 1962, **40**, 1425.
[6] A. Maccoll in "Studies on Chemical Structure and Reactivity," Methuen, London, 1966.
[7] F. P. Herbert, J. A. Kerr, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1965, 5710.
[8] S. W. Benson and G. R. Haugen, *J. Amer. Chem. Soc.*, 1965, **87**, 4036.