358 © 1981 The Chemical Society of Japan *Bull. Chem. Soc. Jpn.*, 54, 358—361 (1981) [Vol. 54, No. 2

The Rate Constants of the Reactions of Hydrogen and Oxygen Atoms with Fluoroethylenes

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(Received May 1, 1980)

The pulse-radiolysis technique combined with the atomic resonance absorption method was used for the measurement of the room-temperature rate constants of the reactions of hydrogen and oxygen atoms with fluoroethylenes. The rate constants obtained at 298±2 K are as follows, in units of 10^{-12} cm^3 molecule^{-1} s^{-1} (1 cm^3 molecule^{-1} s^{-1}=6.022×10^{17} m^3 mol^{-1} s^{-1}). The standard deviation is within 10%.

Atoms	C_2H_4	C_2H_3F	CH_2CF_2	C_2HF_3	C_2F_4
H	1.1	0.52	0.36	0.090	0.082
O	1.0	0.52	0.20	0.63	0.81

The correlation between the rate constants and the reactivity index calculated by the INDO method is discussed.

The determination of the absolute rate constants for the addition of hydrogen and oxygen atoms to monoolefins in the gas phase has been the subject of a number of investigations.[1—6] Although some discrepancies still remain in the temperature dependence, the rate constants at room temperature now appear to be established.

Recently we used the pulse-radiolysis technique for the determination of these rate constants and obtained results consistent with previous measurements.[7—9]

Using the product analysis, Jennings and his collaborators determined the relative rate constants for the addition of hydrogen and oxygen atoms to many fluorinated olefins.[10,11] Moss used a similar technique to measure the relative rate constants of the reactions of oxygen atoms with all the fluoroethylenes.[12] The relative rate constants they reported have an interesting dependence on the number of the substitution of fluorine atoms. In the reactions of hydrogen atoms with fluoroethylenes, the increase in the number of substituted fluorine atoms reduces the relative rate constants, while in the case of oxygen atoms, difluoroethylenes have the lowest reactivity. These results are still open to theoretical interpretation.

We, therefore, attempted the measurement of the absolute rate constants of the reactions of hydrogen and oxygen atoms with some fluoroethylenes, and tried to explain the results theoretically by using the reactivity index calculated by the INDO method.

Experimental

The apparatus used for the measurement of the rate constants has been described previously.[9] The time resolved measurements of hydrogen and oxygen atoms are the same as those described in previous papers.[7,9]

Fluoroethylenes were the products of Daikin Co. After a few freeze-pump-thaw cycles at liquid nitrogen temperature, the middle third was retained. The gas chromatographic analysis using a 2-m Porapak N column at room temperature showed that all compounds contain no detectable impurities.

Results

For the reactions of hydrogen atoms, the H_2 pressure ranging from 180 to 900 Torr (1 Torr=133.3 Pa) was used. No H_2-pressure dependence of the rate constant could be observed. All the decay curves obtained on the oscillograms were of the first-order. Figure 1 summarizes the decay rates obtained as functions of the initial pressure of four kinds of fluoroethylenes. For comparison, the decay rates previously obtained with ethylene are plotted.[7]

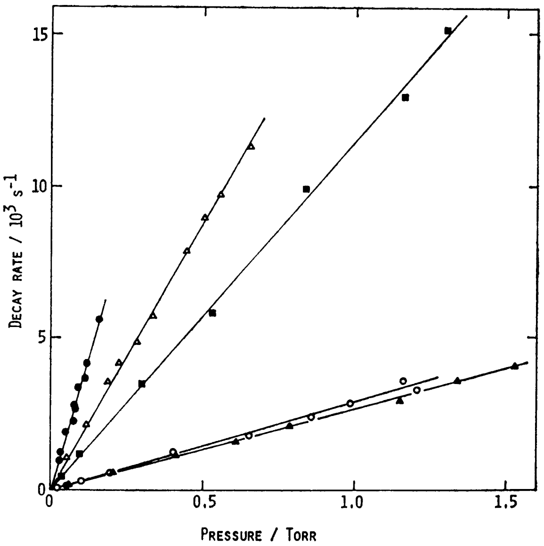

Fig. 1. Plots of the decay rates of hydrogen atoms against reactant pressures.
●: C_2H_4, △: C_2H_3F, ■: CH_2CF_2, ○: C_2HF_3, ▲: C_2F_4.

As the source of oxygen atoms, the mixtures of O_2 (4—10 Torr) and He (100—900 Torr) were used. All the decay curves obtained on the oscillograms were of the first-order. The procedure for the determination of the rate constants of the reactions of oxygen atoms with olefins is the same as that described in the previous paper.[9] Figure 2 summarizes the decay rates obtained as functions of the initial pressure of fluoroethylenes. For comparison, the decay rates previously obtained with ethylene are also plotted.

From the linear plots shown in Figs. 1 and 2, we can calculate the rate constants of the reactions of hydrogen and oxygen atoms with fluoroethylenes. The results are summarized in Fig. 3 as functions of the number of

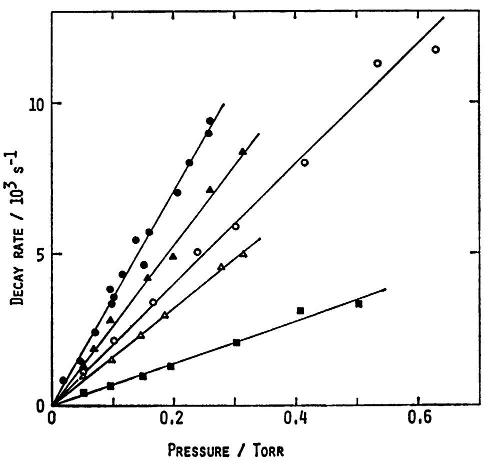

Fig. 2. Plots of the decay rates of oxygen atoms against reactant pressure.
●: C_2H_4, △: C_2H_3F, ■: CH_2CF_2, ○: C_2HF_3, ▲: C_2F_4.

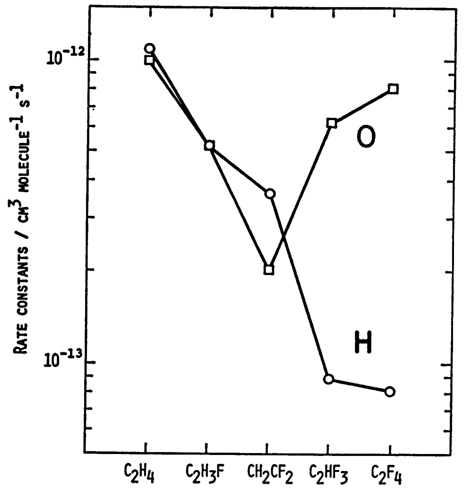

Fig. 3. Comparison of the rate constants of the reactions of H and O atoms with fluoroethylenes.

substituted fluorine atoms.

INDO Calculation

The calculation by the approximate MO theory on fluoroethylenes has already been made by Pople and his colleagues, and the interesting effects of the substitution of fluorine atoms on the charge distribution in the molecules have been discussed.[13] The electron density of the σ-part in the C=C double bond is reduced by the inductive effect of fluorine atoms, while the π-electron density is increased by the so-called mesomeric effect. By performing the INDO calculation, we carefully studied these effects to find if any correlations exist between these electron densities and the rate constants we obtained above, but no clear correlations could be found. The calculation without considering attacking atoms seems to be useless for the discussion on the rate constants. We, therefore, performed the calculation on a model which included the attacking atoms.

According to the recent *ab initio* calculations, when an H atom adds to ethylene, the atom approaches the C atom attached to the double bond from the direction perpendicular to the plane of the ethylene molecule.[14] A similar reaction path has been derived for the addition reaction of O(^{3}P) atom to ethylene,[15,16] although this mechanism seems to be somewhat contradictory to that proposed by Cvetanović.[17] In the present treatment, we assumed that no deformation of the geometry of fluoroethylene molecule occurs during the approach of the attacking atom, and calculated the total energy change as a function of the distance between the attacking atom and the ethylene molecule. The geometry of the calculated model is shown in Fig. 4.

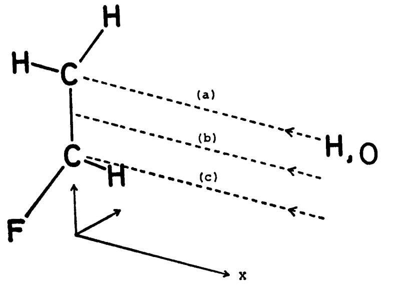

Fig. 4. The geometry used for the INDO calculation.

Among the three calculated reaction paths, the one leading the attacking atom to the C atom which is less substituted by fluorine atoms was found to be the lowest energy path, irrespective of the kind of the attacking atoms. This is consistent with the observations that hydrogen atoms add almost exclusively to the CH_2 group in CH_2CHF and CH_2CF_2,[18] and that oxygen atoms add mainly to the CH_2 group in CH_2CHF.[19] The calculated energy differences, δE, between the total energy change of fluoroethylene, ΔE(fluoroethylene), and that of ethylene, ΔE(ethylene) as functions of the distance, x, between attacking atom and ethylene are shown in Fig. 5. The smaller the value of δE, the more easily can the attacking atoms approach

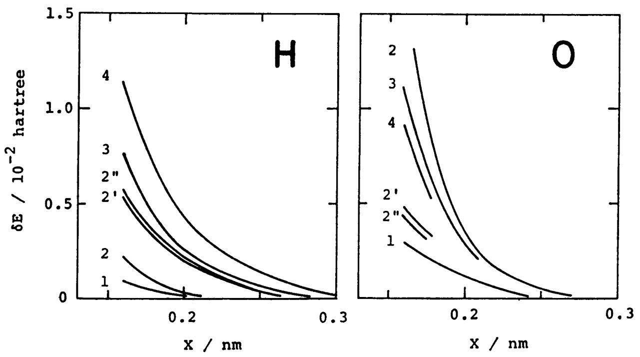

Fig. 5. The energy differences, δE, between the total energy change of fluoroethylene, ΔE(fluoroethylene), and that of ethylene, ΔE(ethylene) in units of hartree (1 hartree=627.51 kcal/mol) as functions of the distance, x, between attacking atom and fluoroethylene, $\Delta E = E(\text{at } x) - E(x \rightarrow \infty)$.[27]
1: C_2H_3F, 2: CH_2CF_2, 2′: *trans*-CHFCHF, 2″: *cis*-CHFCHF, 3: C_2HF_3, 4: C_2F_4.

the fluoroethylene. This property may be called approachability. As Fig. 5 shows, the approachability obtained with H atoms decreases with the increase in the number of substituted fluorine atoms, while that obtained with O atoms has a minimum with CH_2CF_2 molecule.

We can find some correlations between the calculated approachabilities and the rate constants obtained in the previous section. The other obtained with H atoms is in agreement with that of the rate constants. In the case of O atoms, the approachability calculated for C_2H_3F seems to be too large. In spite of the discrepancy, the general trend of the order of the rate constants may be said to be explicable by the calculated approachability.

Discussion

Comparison with Other Investigations. In Table 1, the relative rate constants of the reactions of hydrogen atoms with fluoroethylenes obtained by previous investigations are compared with those calculated from the present data. The results obtained by Kilcoyne and Jennings are in good agreement with our data, although our data are not complete because of the difficulty of obtaining *trans-* and *cis*-1,2-difluoroethylenes. The results of Penzhorn and Sandoval are quite different from those of the others.[20] Since possible reasons for this discrepancy have already been discussed by Kilcoyne and Jennings, it is unnecessary to restate them.

Table 2 compares the absolute rate constants of the reactions of oxygen atoms obtained by Huie *et al.*[21] and Gilbert *et al.*[19] with ours and the relative rate constants reported by Moss.[12] Serious disagreement is observed in the case of C_2F_4. For the reaction of $O+C_2H_3F$, Atkinson and Pitts reported 0.27 ± 0.03 in units of 10^{-12} cm^3 molecule^{-1} s^{-1}.[23] Our result seems to be too large. More extensive investigations on this reaction are now in progress. Recently, Koda discussed the absolute rate constant of the reaction of $O+C_2F_4$.[24] The rate constants he estimated are 0.83 and 1.30 in units of 10^{-12} cm^3 molecule^{-1} s^{-1}. Our result agrees with the smaller value. Further investigations are obviously desirable.

Table 1. Comparison of the relative rate constants of the reactions of H atoms with fluoroethylenes

Compound	PS[a]	KJ[b]	This work
CH_2=CH_2	1.00	1.00	1.00
CH_2=CHF	0.79	0.44	0.47
CH_2=CF_2	1.45	0.36	0.33
trans-CHF=CHF	1.15	0.09	
cis-CHF=CHF	0.70	0.06	
CHF=CF_2	1.65	0.05	0.082
CF_2=CF_2	1.70	0.08	0.075

a) PS: Penzhorn and Sandoval, Ref. 20. b) KJ: Kilcoyne and Jennings, Ref. 11.

Table 2. Comparison of the rate constants of the reactions of O atoms with fluoroethylenes (in units of 10^{-12} cm^3 molecule^{-1} s^{-1})

Compound	HHD	SGG	This work	Moss (Relative)
CH_2=CH_2			1.0	(1.00)[b]
CH_2=CHF	0.436	0.41	0.52	(0.38)
CH_2=CF_2		0.31	0.20	(0.22)
trans-CHF=CHF	0.448[a]	0.58		(0.54)
cis-CHF=CHF		0.37		(0.32)
CHF=CF_2	0.363	0.83	0.63	(0.57)
CF_2=CF_2			0.81	(1.60)

HHD: Huie, Herron, and Davis, Ref. 21; SGG: Slagle, Gutman, and Gilbert, Refs. 19 and 22. a) Mixture of *trans* and *cis*. b) Ref. 12.

Reactivity Index. When Sato and Cvetanović carried out the simple Hückel MO calculation on a series of monoolefins,[25] they anticipated that the calculated parameters such as charge density, bond-order, free valence, or atom localization energy might correlate with the relative rate constants of the reactions of various active species with monoolefins. Actually, the relative rate constants of the reactions of oxygen atoms with monoolefins were found to be well correlated with the excitation energies and bond-orders calculated. When Jennings and Cvetanović determined the relative rate constants of the reactions of hydrogen atoms with a series of monoolefins, they found that these relative rate constants are well correlated with the atom localization energies of the monoolefins.[26] However, when Jennings and his colleagues applied these correlations to the relative rate constants obtained with fluoroethylenes, they failed to find clear correlations.[11] The substitution of fluorine atoms seems to induce an exceptional effect on the molecule.

In the above treatment, the parameters were calculated only on the olefins, one component of the reactants, and the attacking atoms were not included. So, we tried to include the attacking atoms in the calculation, and found some success. We believe that this success is somewhat fortuitous; more extensive investigations are necessary before definite conclusions are drawn from such calculations.

The authors wish to express their thanks to Professor Nobuo Ishikawa of this Institute for the supply of fluoroethylenes, and also to Dr. Kazuo Shimokoshi of this Institute for allowing the use of the program for INDO calculation.

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