Kinetics of the O + F₂ Reaction. A Case of Low Reactivity of Elemental Fluorine

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Abstract: The gas-phase reaction between molecular fluorine and atomic oxygen is studied in a flow system. Oxygen atoms are produced in a microwave discharge. Electron spin resonance detection of oxygen atom decay velocities yields absolute rate constants over the temperature range from 461 to 523 K. A least-squares treatment of the rate data yields the Arrhenius equation $k_1 = 10^{12.99 \pm 0.68} \exp[-10.36 \pm 1.51/RT]$ cm³ mol⁻¹ s⁻¹, where $R = 1.987 \times 10^{-3}$ kcal mol⁻¹ K⁻¹. The variation in activation energy for the O + X₂ reactions (X = halogen) is discussed. The large activation energy for the O + F₂ reaction is attributed to the low polarizability of molecular fluorine.

(I) Introduction

The reactions of atomic oxygen with halogen molecules have been the subject of numerous experimental studies. The earliest investigations, which were conducted in the 1950's, indirectly established lower limits for the room-temperature rates of the O + Cl₂ and O + Br₂ reactions.[2] Subsequent studies on these systems and others in the series have established reaction rates,[3,4] activation energies,[5,6] mechanisms,[4,6-8] and intimate dynamical details of the formation, structure, lifetime, and breakup of the reaction intermediates.[9-12] In this paper we present the first experimental data on the O + F₂ reaction. The rate constant of the reaction is obtained by EPR measurements of oxygen atom decay along a flow tube in the temperature range from 461 to 523 K. These results yield a value of 10.4 kcal mol⁻¹ for the activation energy. We discuss the variation in activation energy for the homologous series of O + X₂ reactions (X = halogen atom) and show that a simple correlation between activation energy and molecular polarizability is consistent with the observed trend.

(II) Experimental Section

A conventional discharge-flow apparatus was employed in these experiments.[13] The flow tube was constructed from thin-wall fused quartz (2.2 cm i.d. by 150 cm length) and passed through an E-235 large access cavity of a Varian E-9 X-band electron paramagnetic resonance spectrometer. A circulating oil bath maintained constant temperature in a 90 cm long section of the flow tube located upstream of the EPR cavity. Thermocouple measurements in the flowing gas indicated that the gas temperature agreed with the thermostat temperature within 2°. The oil temperature was regulated by a mercury contact thermometer (Cenco) which controlled the relay actuated oil heater. A laboratory sump pump (American Instrument Co.) circulated the hot oil. Fluorine was introduced into the thermostated region of the flow tube through the tip of a movable quartz injector (0.9 cm o.d.). The injector inserted coaxially into the upstream end of the flow tube through a custom brass O-ring vacuum coupler. Atomic oxygen was generated in a 0.7 cm i.d. quartz side arm and entered the flow tube approximately 4 cm upstream of the thermostat. A typical Evenson type cavity, powered by a Raytheon-Sorenson PGM-10 microwave generator, was employed as a discharge source of atoms in the side arm. Pressure measurements were made through a side arm located downstream from the EPR cavity with either a DuBrovin or a McLeod gauge. The highly corrosive exhaust gases reacted to form inert CF₄ in a charcoal trap located in the vacuum line between the flow tube and a 150 CFM rotary pump (Stokes 212H-11 MicroVac).

The flow tube and injector were coated with Dupont Teflon Clear Finish 852-201.[13] In preliminary experiments to determine a suitably inert flow tube material, uncoated quartz was tested because high-temperature experiments were anticipated.[14] It was found that above 573 K fluorine reacted with quartz to produce atomic oxygen in sufficient amounts to mask any oxygen atom decay due to gas-phase reaction. Moreover it was shown that at all temperatures investigated the rate of O atom wall recombination on quartz is retarded by the presence of molecular fluorine in the flow tube. Similar effects have been reported previously.[15] This result precluded measurement of O atom decay since the method of analysis rests on the assumption that the change observed in the O atom signal when F₂ is introduced is due solely to gas-phase reaction. A lower recombination rate for atomic oxygen in the presence of fluorine results in an apparent production of atoms. An alumina (Al₂O₃) flow tube passivated with fluorine was tested and found to be chemically inert to fluorine at high temperature, but the oxygen atom recombination rate on alumina was observed to increase rapidly with temperature, and observation of a signal above 348 K was impossible. These difficulties were not present to any serious extent in a Teflon-coated system. The oxygen atom recombination rate on Teflon was negligibly small and unaffected by the presence of fluorine. The recombination rate was also insensitive to temperature variation. The Teflon surface was unstable above 523 K, however, and this limited the temperature range in these experiments. In order to ensure the integrity of the Teflon surface, which was gradually abraded by movement of the injector, reapplication of the finish was necessary after every few experiments. Special preparation of the Teflon surface before each experiment was also required. Exposure of the flow tube and injector surfaces to the atmosphere made reproducible measurements impossible. Therefore the injector was inserted completely into the flow tube and the system was evacuated for at least 12 h before each run. In these experiments the injector motion was restricted to withdrawal in 10-cm intervals to ensure a vacuum clean surface throughout each run.

Fluorine gas (Allied Chemical, 98% purity) from a cylinder located in a metal shed outside the building passed through a NaF trap to remove HF impurity before entering a calibrated capillary flow meter. Stainless steel transfer lines were purged with dry nitrogen between runs and evacuated prior to each experiment. The fluorine flow system was constructed from Pyrex glass, stainless steel, brass, and Teflon and was completely free of any petroleum base lubricants. A small amount of Fluorolube grease (Fisher Scientific GR-90) was used where necessary and Fluorolube oil was used as the manometer fluid. The fluorine flow could be directed either to the injector or to the charcoal trap by means of a three-way valve in the flow manifold. A second capillary flow meter measured an equivalent flow of argon (Linde, 99.66% purity) which was sent through the injector to maintain constant linear velocity when fluorine was directed to the charcoal trap. Argon was chosen as the displacement gas since its viscosity is close to that of fluorine.

Atomic oxygen was produced by two methods in these experiments. In eleven experiments O(³P) was generated in a microwave discharge of O₂ and excess He. Consistent results were obtained in a 12th run, using the rapid titration reaction, N + NO → N₂ + O, as the atom source.[16]

The volume flow rates of all gases were metered at 1 atm of pressure through calibrated capillary flowmeters. Typical flow rates in atm cm³ s⁻¹ for O₂, F₂, and He were 0.075, 1.2, and 8, respectively. Using at least a tenfold excess of F₂ over O₂ ensured that the condition for pseudo-first-order kinetics, [F₂] ≫ [O], was maintained. The helium flow rate was chosen to give the desired linear gas velocity which de-
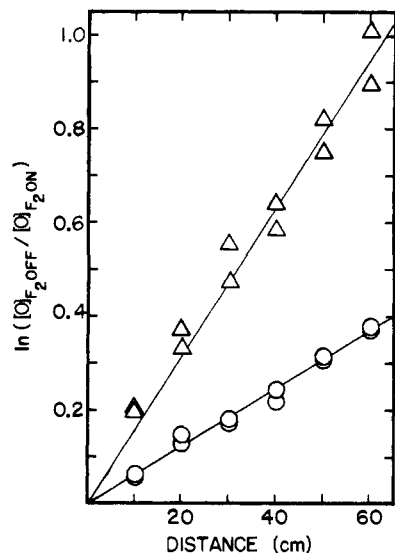
Figure 1. Logarithm of the ratio of the oxygen atom concentrations with the fluorine flow "OFF" and "ON" as a function of the distance from the tip of the injector tube to the downstream end of the thermostat: ($\bigcirc$) T = 461 K, P = 5.25 Torr, linear velocity = 617 cm/s; ($\triangle$) T = 520 K, P = 4.75 Torr, linear velocity = 870 cm/s.

Figure 2. Arrhenius plot of the experimental data: ($\bigcirc$) experiments utilizing the O_2-He discharge source of atomic oxygen; ($\triangle$) experiment in which the $N + NO \rightarrow N_2 + O$ reaction is employed as oxygen atom source.

Table I. Summary of O + F_2 Experiments

Temp, °K	Pressure, Torr	Flow velocity, cm/s	[He] × 10^{10}, mol/cm³	[O_2] × 10^{10}, mol/cm³	[F_2] × 10^{10}, mol/cm³	k_1 × 10^{-8}, cm³/mol/s
461	4.80	557	1430	11.2	228	0.781
461	5.25	617	1603	10.1	213	0.899
462	4.50	613	1299	8.77	254	1.77
475	4.35	637	1250	19.6	199	2.33
476	3.75	687	1080	7.83	175	1.94
477	4.45	873	1331	7.15	158	1.84
493	4.95	583	1365	14.0	231	2.29
502	4.35	703	1193	8.41	188	2.43
511	4.35	651	1157	19.8[a]	188	3.38
520	4.75	870	1323	11.1	131	5.30
520	4.80	722	1296	10.4	174	3.66
523	4.35	874	1182	7.76	144	4.61

[a] Oxygen atoms are produced by the N + NO titration reaction in this experiment. [N_2] = 19.8 × 10^{-10} mol/cm³.
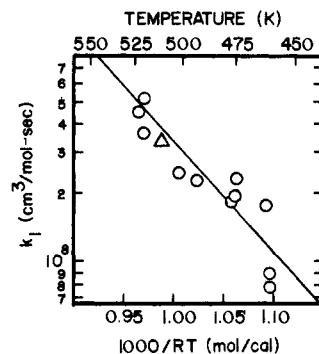
termines the time scale for the decay measurements. Linear flow velocities ranged from 600 to 800 cm s⁻¹. Pressures ranged from 3.75 to 5.25 Torr.

The measurements consist of oxygen atom EPR signal intensities as a function of injector position made at six equally spaced locations along a 50-cm length of the thermostat. At each injector position two signals were obtained, one with F_2 flowing through the injector (denoted $[O]_{F_2(ON)}$) and another with F_2 replaced by Ar (denoted $[O]_{F_2(OFF)}$). As discussed previously[13] the experimental rate constant is obtained from the slope of a semilog plot of $[O]_{F_2(OFF)}/[O]_{F_2(ON)}$ vs. reaction time (or distance).

(III) Results and Mechanism

A preliminary study of the O + Cl_2 reaction was undertaken to test the flow apparatus and experimental procedures. Arrhenius parameters obtained were in agreement with published values[5,6] and are not presented here.

Examples of the measurements for the O + F_2 reaction are shown in Figure 1. The semilog plots are linear as required by the analysis,[13] and the solid curves represent least-squares fits. The experimental conditions and results are summarized in Table I. A comparison of k_1 values obtained at the same

temperature shows some large uncertainties, especially at the lowest temperatures. The scatter is due to interfering surface reactions encountered only in the experiments with fluorine. As mentioned in section II it was possible to minimize surface effects, but not completely eliminate them, by frequently recoating the walls with Teflon and continuously maintaining the flow system at reduced pressure. Despite these measures the surface seemed to act as a minor source or sink for oxygen atoms depending on the daily wall conditions. The oxygen atom decay rate was of course most affected by this at the lowest temperatures where the O + F_2 reaction rate is small.

A standard Arrhenius plot of k_1 is shown in Figure 2. The triangle denotes the experiment in which the titration reaction, $N + NO \rightarrow N_2 + O$, is used as a source of O(^{3}P) which is free of molecular oxygen. Consistent results between the two atom sources support the contention that reactions of vibrationally excited O_2 do not affect the O atom decay rate. A least-squares treatment of the 12 rate-constant data yields the Arrhenius equation,

$$k_1 = 10^{12.99 \pm 0.68} \exp[-10.36 \pm 1.51/RT] \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

where $R = 1.987 \times 10^{-3}$ kcal mol⁻¹ K⁻¹ and T is the absolute temperature. The limits of error are standard statistical uncertainties resulting from the scatter in the data. Weighting factors were not introduced into the least-squares analysis, although as mentioned above the three lowest temperature values of k_1 are less certain than the others.

The mechanism is assumed to be identical with that discussed for the O + Cl_2 and O + Br_2 reactions:[4,6-8]

$$O + F_2 \xrightarrow{k_1} OF + F \qquad (I)$$

$$O + OF \xrightarrow{k_2} O_2 + F \qquad (II)$$
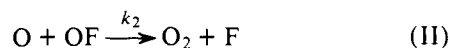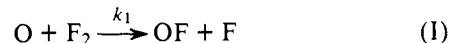
The assumption that $k_2 \gg k_1$ has been justified for the chlorine reaction and should apply also in the fluorine case. Attempts to observe the OF radical in these experiments were unsuccessful. Since k_2 is much greater than k_1, the experimental O atom decay constant k_{exp} is assumed to equal $2k_1$.

(IV) Discussion

This study completes the determination of the rate constants for the reactions of atomic oxygen with the diatomic halogens, F_2, Cl_2, Br_2, and I_2. Activation energies for this series of reactions are presented in Table II. For exoergic atom transfer reactions of the type A· + BC → AB + C· (A· and C· are atoms or free radicals), there have been some successful attempts to correlate activation energies for a series of similar reactions with molecular properties of the separated reactants and products.[17-27] A widely used relationship predicts that acti-

Table II. Thermochemical Data and Activation Energies for the O + X$_2$ → OX + X Reactions

Reaction	Thermochemical data[a]			Activation energies[b]				
				Calcd				
	q	$D^0{}_{XX}$	$D^0{}_{OX}$	A	B	C	D	Obsd
O + F$_2$	13.2	37.5	50.7	−1.1	0.79	4.4	9.6	10.4[c]
O + Cl$_2$	6.3	58	64.3	3.3	3.3	3.3	2.4	3.3[d]
O + Br$_2$	9.9	46.3	56.2	1.0	1.6	2.6	1.6	~1[e]
O + I$_2$	10.5	36.5	47	0.6	0.87	2.0	0.9	~0[f]

[a] q = exoergicity = $D^0{}_{OX} - D^0{}_{XX}$. Bond energies (kcal mol^{-1}) are taken from ref 33-35. [b] Activation energies are expressed in kcal mol^{-1}. Column A: calculated from eq 1 in text; E_0 = 7.32 and γ = 0.639 were obtained by fitting the Cl$_2$ and Br$_2$ data. Column B: calculated from the BEBO formula, eq 2 in text; p = 1.147 was obtained by fitting the Cl$_2$ data. Column C: calculated from eq 3 in text; d = 0.0454 was obtained by fitting the Cl$_2$ data; atomic polarizabilities were taken from ref 36; the following values of α (Å^3) were used: O, 0.77; F, 0.535; Cl, 2.3; Br, 3.4; I, 5. Column D: calculated from eq 4 in text; the slope was obtained by a least-squares fit of eq 4 to the experimental data; see ref 32 for molecular polarizabilities; polarizabilities in Å^3 are: F$_2$, 1.21; Cl$_2$, 4.61; Br$_2$, 6.99; I$_2$, 12.4. [c] This work. [d] References 5 and 6. [e] E_a is estimated from the room temperature rate of ref 4 and an assumed A factor of 10^{13}. [f] Results of molecular beam experiments indicate that E_a is essentially zero. See ref 9.

vation energy should decrease with increasing exoergicity. Two formulas which express this dependence are given in eq 1[17,18,20] and 2[21-24]

$$E_{act} = E_0 - \gamma q \qquad (1)$$

$$E_{act} = (D^0{}_{AB} - q) \left\{ 1 - \left[1 + \left(1 - \frac{q}{D^0{}_{AB}} \right)^{1/(p-1)} \right]^{1-p} \right\} \qquad (2)$$

E_0, γ, and p are empirical parameters; q, the heat of reaction, is positive for exoergic reactions; and $D^0{}_{AB}$ is the bond energy of the product molecule. The results presented in columns A and B of Table II show that the variation in activation energies for the O + X$_2$ reactions cannot be explained by the application of this rule. The fluorine reaction is the most exoergic and yet has the largest activation energy. This conclusion of course depends on the accuracy of the bond strength data. The binding energy of OF has been reviewed,[35] and it is unlikely that the true value could be sufficiently lower than the tabulated value to alter the predicted trend.

One possible explanation for the large activation energy of the O + F$_2$ reaction is based on the reaction dynamics observed in molecular beam experiments on the systems O + I$_2$, Br$_2$, Cl$_2$, IBr, and ICl.[9-12] Experimental results indicate that these reactions proceed via formation and decomposition of an asymmetric collision complex, OXX, which results from a roughly collinear collision between the reactants, and that the complex has a lifetime of several rotational periods ($\geqslant 5 \times 10^{-12}$ s). The structure of the reaction intermediate for each of the systems investigated is consistent with an "electronegativity ordering rule" which states that the preferred geometry of an OX$_2$ triatomic complex has the least electronegative atom in the center.[9,10,28-30] Since the ordering rule predicts an asymmetric OXX complex for all of the halogens except fluorine, the suggestion was advanced that the O + F$_2$ reaction might proceed by insertion of the O atom between the F atoms to form the bent symmetric FOF intermediate and thereby satisfy the "electronegativity ordering rule". Insertion requires a roughly C_{2v} approach of the reactants for which molecular orbital correlations predict a substantial barrier to complex formation. This symmetry imposed potential barrier could account for the large activation energy if the reaction is constrained to proceed by insertion.

We have also considered the possibility that the correlation based on heat of reaction mentioned above does not adequately represent the dependence of activation energy on the molecular properties of the system. Perhaps it overemphasizes the final energy state reached by the products and neglects important
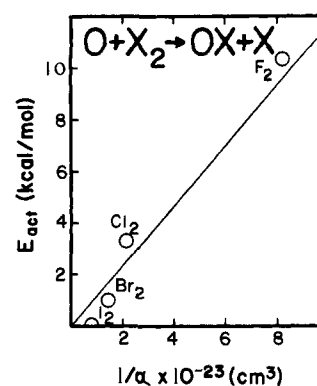
Figure 3. Activation energies from the last column of Table II plotted vs. the reciprocal mean polarizability of the corresponding halogen molecule. Polarizabilities from ref 32.

interactions between the reactants. One parameter that may be a general measure of entrance channel interactions is the polarizability of the reacting species. One may argue that the interaction energy between the reactants at distances characteristic of the onset of reaction will be lowered by attractive dispersion forces the magnitudes of which are proportional to polarizability. An empirical expression which takes into account both the exoergicity of the reaction and the polarizability of the reacting system has been proposed by Spirin.[27] This relationship, presented in eq 3,

$$E_{act} = d(0.75 D_{AC} - q) \left(\frac{1}{P_A} + \frac{1}{P_C} \right) \qquad (3)$$

involves an explicit dependence on the polarizabilities of atoms A· and C· for the reaction, A· + BC → AB + C·. D_{AC} is the bond energy of AC, and d is an empirical parameter. As indicated in column C of Table II the activation energies calculated from Spirin's formula are in qualitative agreement with the observed trend. However, a better quantitative agreement is achieved with a simpler expression which relates activation energy to the polarizability of the halogen molecule as in eq 4.

$$E_{act} = c / \alpha_{X_2} \qquad (4)$$

C is an empirical constant and α_{X_2} is the mean polarizability of the halogen molecule. As shown in column D of Table II and in Figure 3 the calculated and observed values agree within approximately 1 kcal. In the context of this correlation, the variation in activation energy for the O + X$_2$ reaction series can be attributed primarily to a corresponding variation in the

polarizability of the halogens. We have tested this correlation on many series of reactions by plotting activation energy against the reciprocal polarizability of the stable molecular reactant. Near linear plots were obtained for 12 homologous reaction series, including more than 60 atom transfer reactions for which data were available.[31]

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Kinetics of Electron Transfer between the Dimeric Dianions of 1,1-Diphenylethylene and Perylene or Tetracene

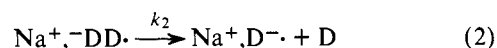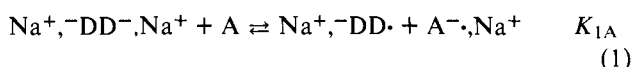## S. Lillie, S. Slomkowski, G. Levin, and M. Szwarc*

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Abstract: Kinetics of the electron transfer initiated reaction taking place in THF between the disodium salt of the dimeric dianion of 1,1-diphenylethylene, $Na^+, \bar{C}(Ph)_2CH_2CH_2\bar{C}(Ph)_2, Na^+ = Na^+, {}^-DD^-, Na^+$, and perylene, Pe, or tetracene, Te, was investigated at ambient temperature by stop-flow technique. It was shown that the studied process involves three steps, namely, $Na^+, {}^-DD^-, Na^+ + Pe$ (or Te) $(k_{-1}) \rightleftarrows Na^+, {}^-DD\cdot + Pe^-\cdot, Na^+$ (or $Te^-\cdot, Na^+$) (k_1) $[K_{Pe} = k_1/k_{-1}$ and $K_{Te} = k_1'/k_{-1}']$, $Na^+, {}^-DD\cdot \rightarrow D + D^-\cdot, Na^+$ (k_2) $(D = CH_2{:}CPh_2)$, and $D^-\cdot, Na^+ + Pe$ (or Te) $\rightarrow D + Pe^-\cdot, Na^+$ (or $Te^-\cdot, Na^+$). The reaction $Na^+, {}^-DD\cdot + Pe$ (or Te) $\rightarrow 2D + Pe^-\cdot, Na^+$ (or $Te^-\cdot, Na^+$) appears to be insignificant and does not contribute to the overall kinetics. The observed kinetics is accounted for by the stationary state approximation $([Na^+, {}^-DD\cdot] \ll [Pe^-\cdot, Na^+])$ with the second step being rate determining. The results led to $k_2K_{Pe} = 0.9 \pm 0.1$ s^{-1}, $k_2K_{Te} = 27 \pm 6$, $k_2/k_{-1} \approx k_2/k_{-1}' \approx 10^{-5}$ M, $k_1 = (2 \pm 1) \times 10^4$ M^{-1} s^{-1}, and $k_1' = (16 \pm 8) \times 10^5$ M^{-1} s^{-1}.

Reduction of 1,1-diphenylethylene, D, by alkali metals yields dimeric dianions, $Ph_2\bar{C}CH_2CH_2\bar{C}Ph_2 = {}^-DD^-$, which may be back-converted into D on reaction with anthracene,[1] A, or pyrene, π, e.g.,

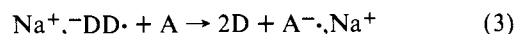$$Na^+, Ph_2\bar{C}CH_2CH_2\bar{C}Ph_2, Na^+ + 2A$$
$$\rightleftarrows 2CH_2{:}CPh_2 + 2A^-\cdot, Na^+$$
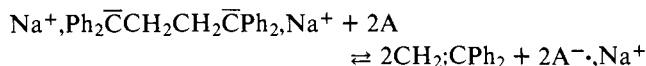
Kinetic results demonstrated that the conversion proceeds in two steps, e.g.,

$$Na^+, {}^-DD^-, Na^+ + A \rightleftarrows Na^+, {}^-DD\cdot + A^-\cdot, Na^+ \qquad K_{1A}$$
$$(1)$$

$$Na^+, {}^-DD\cdot \xrightarrow{k_2} Na^+, D^-\cdot + D \qquad (2)$$

(2) being followed by a rapid electron transfer

$$Na^+, D^-\cdot + A \rightarrow D + A^-\cdot, Na^+$$
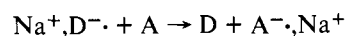
Reaction 3

$$Na^+, {}^-DD\cdot + A \rightarrow 2D + A^-\cdot, Na^+ \qquad (3)$$

which might be expected to contribute to the overall process is not observed. As will be shown later, the spontaneous decomposition of $Na^+, {}^-DD\cdot$ is fast and the hypothetical reaction