tion from the mean for replicate injections of the same sample. Typical values of Φ_{TC} (for example, for the quenching of naphthalene triplets) ranged from 0.55 ([DTBN] = 0.0) to 0.36 ([DTBN] = 0.02 *M*) while the corresponding values of f_{HTC} varied from 0.55 to 0.38.

Photostationary State Measurements. Samples prepared and degassed as above were irradiated either in the apparatus as described or in stationary sample holders having 8-mm windows which fit between the filters and the rotating sample carriage of the apparatus; the use of the stationary sample holders increased the light intensity at the sample by about a factor of 3. Photostationary states were reached after irradiation for *ca.* 24–74 hr, depending on the concentration of DTBN used. Samples containing stilbene were analyzed as above. Analysis of the β-methylstyrenes was also by vpc, using a 6 ft × 0.25 in. column of 6% polyphenyl ether on Anachrom ABS at 125°. Selected samples were tested for loss of DTBN to side reactions by monitoring the absorbance of the DTBN at 465 nm[20] with a Cary 14 spectrophotometer before and after irradiation.[41]

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Comments on the Pyrolysis Kinetics of Oxygen Difluoride

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Abstract: The validity of conclusions reached using data obtained from a shock tube kinetic study of the pyrolysis of OF_2 is discussed and the assertion that the differences between shock tube and conventional flow and static system results for this reaction are due to surface effects is examined.

The objective of this publication is to critically review the treatment of the shock tube data made by Lin and Bauer in their reported[1] kinetic study of the pyrolysis of OF_2 and to discuss the validity of their assertion that for this reaction the differences in the kinetic results obtained in conventional static or flow systems are due primarily to surface effects.

Considering the latter point first, it is agreed that investigators of reaction rates using conventional systems must be cautious of the possibility of surface contributions, while shock tube studies are relatively free of this complication. However, if the results from the two types of studies do not agree, it is believed that the conventional system results should not be automatically discounted without additional evidence that the surface contributions are significant. There are numerous examples in the literature in which surfaces have been rendered relatively unreactive, for example: the carbonizing of glass reactor walls during the pyrolysis of pentachloroethane[2] allowed the study of the homogeneous reaction, as evidenced by a change in the surface area/volume ratio of about a factor of 10; or in the case of fluorine containing compounds, the passivating of monel reactor walls essentially eliminated the heterogeneous reaction in the pyrolysis of poly(difluoroamino)fluoromethanes[3] as shown by a change in the surface area/volume ratio of a factor of 8 and by comparing rates obtained from uncoated and Teflon coated reactors.

Specifically, the evidence as to the homogeneity of the OF_2 pyrolysis appears reasonably conclusive because of the following observations.

(a) All of the conventional studies used different reactor materials, aluminum,[4] nickel,[5] monel,[6] and magnesium and several types of glass.[7] It appears extremely unlikely that all of these surfaces would quantitatively affect the pyrolysis rate the same. However, the rates from these static and flow system studies are fairly consistent.

(b) Two studies did increase the surface area of the aluminum and monel reactors by factors of 2 and 2.5, respectively; again no significant change in the rate was observed. It is realized that larger changes in surface area are desirable (in the case of the monel reactor it was not possible); however, this observation when coupled with those described in (a) and (c) strengthens the conclusion that the reaction is homogeneous in conventional systems. In addition, it is acknowledged that a surface may change the rates of both initiation and termination steps such that the overall reaction rate is apparently unaffected by the surface, but it is believed that this situation is the exception rather than the rule for surface reactions.

(c) Generally, surface reactions have lower activation energies than the corresponding homogeneous reactions.[8] Thus, when heterogeneous and homogeneous reactions compete, surface contributions are expected to be relatively lower at higher temperatures. Comparison of the rate constants (Figure 1 of ref 1) and including those obtained in the most recent flow study[6] shows that the accumulated data obtained from all of the conventional systems run about parallel in an Arrhenius plot to that obtained by Lin and Bauer using

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the shock tube. Some of the individual studies may show lower activation energies; *e.g.*, Solomon, *et al.*, reported values as low as 30 and 31.5 kcal/mol in static[4] and shock tube[9] experiments, respectively. However, all of the data from the flow and static systems encompass a much larger temperature range and as a group are consistent with the value of 38 kcal/mol as reported by Lin and Bauer. Thus, it appears that the activation energies of the reaction in conventional systems and in shock tubes are about the same and that any differences in rate constants would be in the frequency factor, which is extremely improbable according to absolute reaction rate theory.[8]

The conclusion would have to be drawn that since the shock tube results are about a factor of 5 lower than those obtained in the low-pressure flow system,[5] or than extrapolations of those obtained in the other conventional systems, the overwhelming majority of the reaction observed in the latter system is heterogeneous. However, the rate of the reaction is unaffected by the amount or nature of the surface present, and the relative heterogeneous and homogeneous contributions to the rates are independent of temperature. The contention that the discrepancies between conventional and shock tube kinetic results for the pyrolysis of OF_2 are due to surface effects is considerably weakened by these observations.

The second point to be considered is the apparent temperature independence of the observed rate constant, k_{obsd}, above about 1000°K that was reported in ref 1 (an observation which is inconsistent with those of the other shock tube studies[9,10]). The k_{obsd} was defined by the following equation

$$k_{obsd} = [(M)t]^{-1} \ln (OF_2)_0/[(OF_2)_0 - 2(O_2)_t]$$

which assumes that the overall stoichiometry was applicable at experimental conditions since only the product oxygen was measured quantitatively. This leveling off of the Arrhenius plot was attributed by Lin and Bauer to an approach to equilibrium of the initiation step in the mechanism

$$OF_2 + M \longrightarrow OF + F + M \qquad (1)$$

The importance of this postulation lies in these authors' reliance on this equilibration to render the oxygen production insensitive to k_1 and directly proportional to k_2 for the purpose of calculating k_2.

$$2OF \longrightarrow O_2 + 2F \qquad (2)$$

However, the validity of the data above 1000°K can be questioned; *i.e.*, if the postulated mechanism and assumed rate constants which lead to the predicted concentration profiles (ref 1, Figure 3) are correct, then the rate of oxygen formation is not a reliable measure of the rate of disappearance of OF_2. The data (ref 1, Table I) indicate a leveling off of the extent of reaction at about 75–90% of reaction (two points are above 90%, but both are above 1200°K) over wide temperature and dwell time ranges and with a very large scatter in the points. From Figure 3 of ref 1 it can be seen that the predicted extents of reaction at 1020°K appear close to that range under the conditions used, but more importantly, as the temperature increases the predicted extent of reaction, based on OF_2 disappearance, and the measured oxygen concentration becomes completely inconsistent. For example, at 1390°K and 5 μsec the OF_2 is predicted to be better than 99% consumed, but all data were obtained at greater than 500 μsec. Thus, the discrepancy at the higher temperature in oxygen produced and OF_2 consumed because of an apparent lag in the rate of oxygen formation restricts the use of the previous equation for k_{obsd} to data below 1020°K, and invalidates the evidence for the apparent equilibration for step 1.

Another consideration is the prediction that the OF radical concentration is the same order of magnitude as, and under certain conditions larger than, the oxygen concentration at all temperatures and reaction times used. Thus, if these concentrations were correct, considerable amounts of recombination, disproportionation, etc., would have to occur during the quench period before analysis, resulting in a greater uncertainty in the significance of the observed rate constant at temperatures below 1020°K. Even the direct measurement of the OF_2 concentration, rather than that of oxygen, will not eliminate this problem. Only if the reverse of step one does not occur during the quench, will the calculated k_{obsd} be representative of the rate of disappearance of OF_2 at the reaction temperature.

From this discussion it can be concluded that either the postulated mechanism by Lin and Bauer and the estimated rate constants for those steps are not correct or that k_{obsd} is not representative of the pyrolysis rate, or both. The more recent shock tube study by Henrici, Lin, and Bauer[11] of reactions of OF_2 does not significantly change the above discussion. Furthermore, it should be noted that caution must be exercised in the study of kinetics as to the extents of reaction examined; those which are too high will result in large experimental uncertainties and possible complications from side reactions.

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