Kinetics of Hexafluoropropylene Oxide Pyrolysis Studied by Gas-Phase NMR. Kinetic Measurements Made Easy[†]

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Abstract. Gas-phase NMR complemented with a high-temperature probe makes possible quantitative kinetic studies of homogeneous vapor-phase reactions with unprecedented ease, as demonstrated with a study of the thermal fragmentation of hexafluoropropylene oxide. The reaction follows strictly first-order kinetics, is unaffected by surface chemistry, and the resulting Arrhenius activation parameters compare well with those obtained by more laborious classical methods of gas-phase reaction kinetics. The fragmentation kinetics is also unaffected by the presence of oxygen. The profiles for the evolution of the final products in this case show very graphically that singlet difluorocarbene, one of the initial products of the fragmentation of hexafluoropropylene oxide, does not react with oxygen, a ground-state triplet, at chemically significant rates.

INTRODUCTION

We have recently shown that gas-phase NMR, wellestablished for physical studies¹ but singularly overlooked for reaction kinetics,² could be used to follow the kinetics of hydrogenation of simple fluoroolefins, e.g., perfluoro-2-pentene, over palladium supported on alumina.3 We argued that gas-phase NMR represents a powerful new technique for heterogeneous catalysis. Now we demonstrate that with the addition of a commercial high-temperature probe with an upper temperature limit of 400 °C, gas-phase NMR makes possible quantitative kinetic studies of homogeneous vaporphase reactions with unprecedented ease, dispelling the firmly entrenched idea that quantitative kinetics requires tedious and time-consuming effort. Kinetic measurements are often crucial to optimize synthetic procedures, to establish reaction mechanisms, or to improve industrial processes involving vapor-phase chemistry. They are now made easy largely because of the automation of modern NMR spectrometers that allows the unattended acquisition of spectra according to a predetermined time schedule and the automatic processing of a large number of spectra. We have chosen for this demonstration the kinetics of the thermal decomposition of hexafluoropropylene oxide because the activation parameters for its thermal decomposition have been determined by classical methods of gas-phase kinetics,⁴ allowing an assessment of the validity of the new methodology.

Although in the present work we use fluorine NMR detection, we routinely carry out gas-phase NMR studies using proton detection. Fluorine detection has certain advantages for gas-phase work, however, because of very short longitudinal relaxation times T_1 , caused by spin-rotation relaxation, of the order of tens of milliseconds for fluorines observed in the vapor phase compared to approximately 1 s for protons. The short T_1 's allow fast signal averaging (hundreds of transients in less than a minute) to regain the signal-to-noise ratio lost by linebroadening in the vapor phase and fast acquisition of kinetic data. Because of the high-temperature probe, gas-phase NMR for chemical reaction kinetics is not limited to substances that are gases at room temperature, but can be used with liquids above their boiling point and even solids with either substantial vapor pressures at elevated temperatures or that evolve volatiles on heating.

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Hexafluoropropylene oxide (HFPO) is a key intermediate for the fluoroproducts industry.⁵ It is used, inter alia, for the manufacture of inert oligomeric fluoroether fluids (Krytox[®]) and for the production of perfluorovinylether monomers essential for the modern fluoropolymer industry. It is a colorless gas with a boiling point of ca. -27 °C, completely stable at room temperature. Above ~150 °C, however, it undergoes a unimolecular fragmentation producing difluorocarbene, CF₂, in its singlet electronic state,^{6,7} and trifluoroacetyl fluoride (eq 1).⁸ The major products of this pyrolysis are tetrafluoroethylene (TFE), produced by recombination of two difluorocarbenes, and perfluorocyclopropane (PFCP) arising by addition of a CF₂ carbene to TFE (eq 2).

$$2 : CF_2 \longrightarrow CF_2 = CF_2 \xrightarrow{: CF_2} F_2C \xrightarrow{: CF_2} F_2C \xrightarrow{: CF_2} (2)$$

TFE PFCP

The pyrolysis of HFPO is indeed an excellent source of difluorocarbenes for various synthetic purposes. For example, it has found applications in the synthesis of various fluorocyclopropanes,⁹ as a route to fluorinated polymers by difluorocarbene addition to polydienes,¹⁰ as a method of growing $(CF_2)_n$ thin films on various surfaces for electronic applications,¹¹ and to produce new fluorinated materials by multiple addition of difluorocarbenes to the double bonds of fullerenes.12 Compared to carbene itself, CH₂, a ground-state electronic triplet, difluorocarbene is strongly stabilized in the singlet state, and therefore much less reactive, by the back donation of lone-pair electron density on the α fluorine into the the empty π -orbital of the carbene center, as shown below. This stabilization is also responsible for the reversibility of the CF, addition to TFE (eq 2) so that, at sufficiently elevated temperatures, PFCP itself becomes a useful source of difluorocarbenes.¹³

In the published kinetic study of the pyrolysis of HFPO,⁴ rate constants were obtained by the time-honored method of following the rate of pressure increase in a 500-cc Monel or Pyrex bulb containing HFPO at



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certain initial pressures (10 to 100 Torr) and submerged in a molten salt bath in the temperature range 140 °C to 260 °C. The method is not easy to apply since the composition of the gas, that is, the relative amounts of TFE and PFCP, must be known at each time point and account must be made of any loss of CF₂ carbenes through polymerization. The following Arrhenius activation parameters were obtained: $E_a = 36.3$ kcal/mol and log(A) = 13.2. The activation energy for the thermal decomposition of HFPO was also estimated in two studies concerned primarily with the chemical vapor deposition of $(CF_2)_n$ films.^{12,14} In the first, the rate of $(CF_2)_n$ film deposition was followed as a function of the temperature of a hot filament over which HFPO thermally decomposed, while in the second, the intensity of the fluorescence excitation spectrum of CF₂ carbenes exiting a pyrolysis nozzle was measured at different nozzle temperatures. The reported values of 29 kcal/mol and 31 kcal/mol, respectively, are undoubtedly too low since they are quite close to the Arrhenius activation energy reported for the homogeneous thermal fragmentation of tetrafluoroethylene oxide¹⁵ (31.6 kcal/mol, log(A) = 13.7), which proceeds at lower temperatures (120 °C to 140 °C) than that of HFPO. In the latter study, the kinetics was followed either by ex situ gaschromatographic analysis or infrared spectrophotometry.

EXPERIMENTAL SECTION

The NMR reaction vessel is an ampoule made from a short section of a 10-mm NMR tube with a coaxial 5-mm tube extension to allow quick attachment to a high-vacuum system via an O-ring adapter for sealing NMR tubes (Fig. 1). The gasphase NMR ampoules are now available commercially at low cost (New Era Enterprise, Vineland, NJ 08360-0425). Gases are metered using the ideal gas law by isolating a 53-mL bulb with the appropriate pressure measured with an MKS Baratron capacitance pressure transducer, followed by bulb-to-bulb transfer. Oxygen is introduced semiquantitatively by measuring the pressure drop in the vacuum manifold of known volume when the stopcock isolating the ampoule kept in liquid nitrogen is carefully partially opened. Because oxygen has a finite vapor pressure at the temperature of liquid nitrogen, some of it is left behind when the ampoule is sealed with a propane torch. When all gaseous reactants and any internal standard gas (typically inert CF_4) are loaded, the ampoule is sealed off with a flame at its neck so as to leave a short stub which facilitates the attachment of the ampoule to a matching stub of the sample holder by means of a short piece of heatshrink Teflon® tubing (Fig. 1). The latter is surprisingly effective even at probe temperatures close to 400 °C, where it softens but continues to hold the ampoule. The main purpose of a short ampoule is to ensure that the reacting system is at a reasonably constant temperature, although we measure temperature gradients of 2-3 °C inside the ampoule (vide infra).



Fig. 1. Diagrams of the gas-phase NMR ampoule attached to a vacuum system before being sealed off with a propane torch (left) and seated in a commercial high-temperature NMR probe (right).

Caution: Great attention must be paid not to create excessive pressures in sealed ampoules at elevated temperatures.

A safe upper limit of 250 µmol of volatiles is obtained from the ideal gas law with an ampoule volume of 3.8 mL and with a safe internal pressure of 3 atm at 400 °C, as repeatedly observed in our hands. Consideration must also be given to the stoichiometry of the vapor-phase reactions. In the present work, the ampoules were loaded with 78 µmol of pure HFPO and 78 µmol of CF₄ (both DuPont products), with the latter serving as inert diluent and internal concentration and chemical shift standard ($\delta = -63.5$ ppm, assumed temperature-independent). Together these materials generate an ampoule internal pressure of 1 atm at 25 °C and 1.6 atm at 200 °C by the ideal gas law. The ampoules were thoroughly dried in a vacuum oven to minimize the reaction of CF3COF with adsorbed water, with concomitant generation of HF. Production of the latter causes etching of the ampoules and is indicated by the detection of SiF₄($\delta = -167.7$ ppm). Only traces of the latter were observed with dried ampoules.

The high-temperature probe is a commercial¹⁶ 10-mm probe for a 300-MHz wide-bore magnet with an upper temperature limit of 400 °C. Heating is achieved by flowing into the probe hot nitrogen gas whose temperature is regulated by a

controller. Another nitrogen flow in an anular space is used for cooling the probe externals and the exiting hot gas in the upper stack. The probe comprises also a cylindrical Macor ceramic head which thermally seals the heated probe compartment and which accepts a flanged 10 mm OD by 8 inch Pyrex test tube. Our ampoule arrangement in effect duplicates the 10 mm by 8 inch test tube provided with the high-temperature probe, departing from its geometry only by having a break in the middle where the ampoule and the necked-down upper tube, flanged exactly as the original test tube to fit into the Macor head, are joined by the Teflon® sleeve (Fig. 1). The latter allows minor adjustments in the total length so that the bottom of the ampoule is at exactly the same depth as the manufacturer's test tube bottom to insure reproducibility of the internal temperature. The latter was measured with a thin thermocouple positioned in the center of a dummy ampoule identical to those used for actual kinetic runs except for a small hole at the end of the 5-mm stub. Measurements were carried out for different flow rates of both the heating and cooling nitrogen streams, as well as with different positioning of the thermocouple tip along the axis of the dummy ampoule in order to map out the temperature inside the probe. For the nitrogen flows used in this work, the temperature in the center of the ampoule (at 1 atm air) is given as a function of the temperature read by the external thermocouple T(set) by the expression $T(^{\circ}C, corr.) =$ $T(\text{set}) + 1.907 - 2.21 \times 10^{-2} T(\text{set}) - 3.618 \times 10^{-5} T(\text{set})^2$ valid for 75 °C > T(set) > 375 °C. Thus, a correction of -4 °C must be applied for a set temperature of 200 °C and -5 °C at 230 °C. Repeated calibrations indicate that the temperature in the ampoule is defined within 1 to 2 °C. To initiate a kinetic run, the Macor head carrying the sample assembly is pneumatically lowered into the probe kept at the desired temperature. Automatic NMR data acquisition starts as soon as the sample is seated in the probe according to a script that defines the time steps in the repetitive spectral sampling.

The spectra are obtained with a GE NMR Instruments Omega 300 spectrometer using a SunOS Release 4.03e operating system based on a Sparc-1 computer. No field lock is used, and the ampoules are not spun. A small flip angle of the magnetization vector (typically 10°-15°) is used for a more uniform power distribution over the wide ¹⁹F NMR spectral widths. Very short pulse delays of 50 ms allowed the acquisition of 512 transients in about 1 min.

RESULTS AND DISCUSSION

The gas-phase ¹⁹F NMR spectrum of a 1:1 molar mixture of HFPO (78 µmol) and CF₄ (78 µmol) as diluent and internal standard at approximately 1 atm total pressure before reaction at 25 °C is shown in Fig. 2. The resonance for CF₄ is exceptionally broad (150 Hz) because of its spherical shape and relatively small moment of inertia. The four main absorptions for HFPO are assigned as indicated in Fig. 2 ($\delta = -78.2$ ppm (CF₃, $\Delta v_{1/2} \sim 30$ Hz), -111.4 ppm, -114.9 ppm, and -158.0 ppm).¹⁷ The resonances for the unique fluorines are broader than the CF₃ fluorine resonance because of



Fig. 2. Gas-phase ¹⁹F NMR spectra of a 1:1 molar mixture o hexafluoropropylene oxide and CF_4 at 1 atm total pressure a 25 °C before reaction (top) and after 20 min at 215 °C (bottom)

unresolved splittings. The spectrum acquired after 20 min at 215 °C (Fig. 2) shows the loss of HFPO¹⁸ and the formation of the main products of decomposition CF₃COF (δ = 12.9 ppm and -74.9 ppm (CF₃)), TFE (δ = -134.7 ppm), and PFCP ($\delta = -158.5$ ppm ($\Delta v_{1/2} \sim$ 20 Hz). The time dependence of the normalized intensities (for a single fluorine) of the CF_3 resonances for HFPO and CF₃COF is plotted in Fig. 3 together with the intensity of the CF₄ absorption normalized (for a single fluorine) to 100. The latter is invariant with time since CF_4 is inert under the reaction conditions. Points acquired in the first 3-4 min are discarded since the ampoule is not yet at thermal equilibrium.¹⁹ The time evolution of the normalized intensities for TFE and perfluorocyclopropane (for a single fluorine) are also shown in Fig. 3. While the shape of the TFE and PFCP profiles are reliable and chemically significant, the intensities are not exactly comparable to those of HFPO and CF₃COF in Fig. 3. This is because of the gradual drop in RF power, and therefore signal intensity, away from the central region of the spectrum where the carrier frequency was placed (between the CF₃ fluorine resonances of HFPO and CF₃COF). Corrections for this effect can be carried out when needed.

Both the disappearance of HFPO and the appearance of CF_3COF follow strictly first-order kinetics and can be



Fig. 3. Reaction profile for the thermal decomposition of 78 μ mol hexafluoropropylene oxide at 215 °C in the presence of 78 μ mol inert CF₄ diluent and internal standard. The points for HFPO and CF₃COF were least-squares fitted by simple exponential functions appropriate for first-order kinetics.

fitted by simple exponentials to obtain the first-order rate constants (Fig. 3). The experiment was repeated at different temperatures, and the strict first-order behavior for the disappearance of HFPO at these temperatures is shown by the linearity of the ln([HFPO] / [HFPO]₀) vs. time plots in Fig. 4. The slopes of these lines give the following rates: $6.827 \times 10^{-5} \text{ s}^{-1}$ (190 °C), $3.348 \times 10^{-4} \text{ s}^{-1}$ (210 °C), $8.100 \times 10^{-4} \text{ s}^{-1}$ (220 °C), and $1.805 \times 10^{-3} \text{ s}^{-1}$ (230 °C). An Arrhenius plot using these data gives an Arrhenius activation energy $E_a = 37.9$ kcal/mol and log(A) = 13.7. The Arrhenius plot (Fig. 4) obtained by applying the temperature correction discussed in the Experimental Section yields the slightly different activation parameters of $E_a = 38.7$ kcal/mol and log(A) = 14.2. An Eyring plot of the same data yields the follow-



Fig. 4. Semilog plots showing the first-order kinetics of the thermal fragmentation of hexafluoropropylene oxide and the Arrhenius plot obtained from the corresponding rate constants. The temperatures used for the Arrhenius plot have been corrected for the temperature gradient in the NMR probe.

ing activation parameters: $\Delta G^* = 36.0 \text{ kcal/mol}, \Delta H^* = 37.8 \text{ kcal/mol}, \Delta S^* = 3.8 \text{ e.u.}$ The major source of error is clearly the uncertainty in the temperature and the slight temperature gradient in the ampoule (see Experimental Section). An idea of the possible error in E_a can be had by comparing the values obtained with and without the temperature correction (37.9 kcal/mol vs. 38.7 kcal/mol). We consider, therefore, that the activation energy is known well within $\pm 1.0 \text{ kcal/mol}$.

Our activation parameters, with or without the temperature correction, indicate slightly slower kinetics than was obtained by pressure measurements⁴ ($E_a = 36.3 \text{ kcal/mol}$, log(A) = 13.2). This is surprising since the opposite would have been anticipated by possible catalysis by the glass walls (potentially more important

in a reactor of only 3.8 mL volume compared to one of 500 mL volume). We exlude wall catalysis since we obtained exactly the same rate of HFPO disappearance at 200 °C in experiments in which we deliberately added 100 mg of crushed ampoule glass to the ampoule reactor. Indeed, neither the addition of 100 mg of powdered nickel metal as a potential catalyst to the bottom of the ampoule nor the addition of approximately two equiv of oxygen had any measurable effect on the rate. We conclude, therefore, that we are measuring the rate of a homogeneous unimolecular decomposition unaffected by surface or other kind of chemistry. The discrepancy is probably due to the presence of a buffer gas in our work and to the different initial pressures of HFPO, which are higher in our case to obtain satisfactory signal-to-noise ratios but also to bring us closer to practical synthetic chemistry where accurate rates are needed for optimization of chemical processes.

Our study of the thermal decomposition of HFPO in the presence of two equiv of oxygen at 210 °C (Fig. 5) illustrates the value of reaction profiles for the various reaction components, easily obtainable by gas-phase NMR, for mechanistic considerations even when these profiles are not entirely calibrated to reflect accurate concentrations in the vapor phase because of problems associated with uneven RF power distribution over the entire width of the spectrum or with different T₁ relaxation times for different resonances, both of which can be dealt with. In this decomposition, where HFPO disappears at exactly the same rate as it would disappear without added oxygen and where the formation of CF₃COF is also unaffected, a new fluorine resonance appears at $\delta = -26.3$ ppm with a kinetic profile (normalized for a single fluorine but uncalibrated), shown in Fig. 5 belonging to carbonyl fluoride (COF₂). The addition of oxygen profoundly affects the profiles for the formation of TFE and PFCP, as can be seen by comparing the bottom panels of Figs. 3 and 5. The mechanistic question arises of how carbonyl fluoride is formed. Since difluorocarbene, in spite of its stabilization mentioned above, is still a short-lived intermediate born in this case surrounded by oxygen molecules, one might imagine that the first step in the formation of COF₂ is the union of difluorocarbene with oxygen to form an intermediate CF₂OO which might be a diradical²⁰ or even a cyclic difluorodioxirane.²¹ Comparison of the reaction profiles for TFE formation in the absence (Fig. 3) and presence of oxygen (Fig. 5), however, excludes any appreciable direct reaction of difluorocarbene with oxygen since the initial rate of formation of TFE is practically unchanged by the presence of oxygen. In other words, although surrounded by oxygen molecules, CF₂ carbenes in very low concentrations (no detectable



Fig. 5. Reaction profiles for the thermal decomposition of 78 μ mol hexafluoropropylene oxide at 210 °C in the presence of 2 equiv oxygen. The points for HFPO and CF₃COF are least-squares fitted by simple exponential functions appropriate for first-order kinetics.

NMR absorption) have the time to dimerize to form TFE. Carbonyl fluoride must then be formed by subsequent reaction of TFE with oxygen and, accordingly, the concentration of TFE goes through a maximum to drop down to zero as the reaction progresses (Fig. 5). The drop in perfluorocyclopropane concentration in Fig. 5 is also related to the reaction of TFE with oxygen since, as was noted above, perfluorocyclopropane itself decomposes thermally to TFE and difluorocarbene with known kinetics.²² The TFE formed by this route will also react with oxygen causing the consumption of perfluorocyclopropane. The low reactivity of singlet CF₂ carbene has been noted before in flash photolysis studies²³ and is an example of a spin-forbidden reaction since excited triplet CF2 does react readily with oxygen.8 Our gas-phase NMR results underscore the value of

detailed kinetic reaction profiles, so easily obtainable by our technique, in providing chemical, kinetic, and mechanistic information that would be very laborious to obtain by other means.

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REFERENCES AND NOTES

- For reviews, see (a) Govil, G. Appl. Spectrosc. Rev. 1973, 7, 47. (b) Harris, R.K. Org. Magn. Reson. 1983, 21, 580. (c) Armstrong, R.L. Magn. Reson. Rev. 1987, 12, 91. (d) Jameson, C.J. Chem. Rev. 1991, 91, 1375. (e) Jameson, C.J. In Encyclopedia of NMR, Grant, D.M.; Harris, R.K., Eds.; Wiley: New York, 1996; Vol. 4, p 2179. (f) True, N.S. In Encyclopedia of NMR, Grant, D.M.; Harris, R.K., Eds.; Wiley, New York, 1996, Vol. 4, p 2173. (g) LeMaster, C.B. J. Prog. Nuclear Magn. Spectrosc. 1997, 31, 119.
- (2) (a) Haugh, M.J.; Dalton, D.R. J. Am. Chem. Soc. 1975, 97, 5674. (b) Costello, F.; Dalton, D.R.; Poole, J.A. J. Phys. Chem. 1986, 90, 5352.
- (3) (a) Kating, P.M.; Krusic, P.J.; Roe, D.C.; Smart, B.E. J. Am. Chem. Soc. 1996, 118, 10000. (b) Roe, D.C.; Kating, P.M.; Krusic, P.J.; Smart, B.E. Top. Cat. 1998, 5, 133.
- (4) Kennedy, R.C.; Levy, J.B. J. Fluorine Chem. 1976, 7, 101.
- (5) For a review of its chemistry, see Millauer, H.; Schwertfeger, W; Siegemund, G. Angew. Chem., Int. Ed. Engl. 1985, 24, 161.
- (6) For a review of fluorinated carbene chemistry, see Brahms, D.L.S.; Dailey, W.P. Chem. Rev. 1996, 96, 1585.
- (7) Triplet difluorocarbene lies 56.6 kcal/mol above the singlet ground state (Koda, S. Chem. Phys. 1982, 66, 383) and has different chemistry (e.g., Heicklen, J.; Cohen, N.; Saunders, D. J. Phys. Chem. 1965, 69, 1774).
- (8) (a) Moore, E.P., Jr. U.S. Pat. 1967, 3,338,978. (b) Mahler, W., Resnick, P.R. J. Fluorine Chem. 1973, 3, 451.
- (9) (a) Sargeant, P.B. J. Org. Chem. 1970, 35, 678. (b) Smart, B.E. In Chemistry of Organic Fluorine Compounds II, Hudlicky, M.; Pavlath, A.E., Eds.; American Chemical Society, Washington, DC, 1995.
- (10) (a) Cais, R.E.; Siddiqui, S. Macromolecules 1986, 19, 595. (b) Thomsen, M.W. Macromolecules 1991, 24, 6343. (c) Ren, Y.; Lodge, T.P.; Hillmyer, M.A. J. Am. Chem. Soc. 1998, 120, 6830.
- (11) e.g., Limb, S.J.; Labelle, C.B.; Gleason, K.K.; Edell, D.J.; Gleason, E.F. Appl. Phys. Lett. **1996**, 68, 2810.
- (12) Krusic, P.J.; Yang, Z.-Y. Unpublished work.
- (13) Birchall, J.M.; Fields, R.; Haszeldine, R.N.; McLean, R.J. J. Fluorine Chem. 1980, 15, 487.
- (14) Knickelbein, M.B.; Webb, D.A.; Grant, E.R. Mater.

Res. Soc. Symp. Proc. 1985, 38, 23.

- (15) Lenzi, M.; Mele, A. J. Chem. Phys. 1965, 43, 1974.
- (16) NALORAC Corporation, 841A Arnold Drive, Martinez, CA, 94553, email: sales@nalorac.com.
- (17) Ruff, J.K.; Merritt, R.F. J. Org. Chem. 1965, 30, 3968.
- (18) The fluorine chemical shifts of HFPO are slightly temperature dependent. At 215 °C they are: -77.2 ppm (CF₃), -110.9 ppm, -114.5 ppm, -156.4 ppm measured relative to CF₄ (-63.5 ppm) assumed temperature independent.
- (19) The NMR resonances detected in this period, when the temperature in the ampoule is changing rapidly, are broad and ill-shaped because they move during signal acquisition as a result of the temperature dependence of their chemical shifts. Furthermore, they cannot be com-

pared with those obtained at thermal equilibrium since NMR intensities vary inversely with temperature (Curie law). With reagents that are liquid at room temperature, the situation is even worse since in the first few minutes the internal vapor pressure, and therefore the signal strength, changes rapidly as the temperature is rising.

- (20) Davis, S.R.; Yu, B. J. Phys. Chem. 1996, 100, 11276.
- (21) Kraka, E.; Konkoli, Z.; Cremer, D.; Fowler, J.; Schaefer, H.F. III J. Am. Chem. Soc. 1996, 118, 10595.
- (22) Atkinson, B.; McKeagan, D. J. Chem. Soc., Chem. Commun. 1966, 189.
- (23) (a) Dalby, F.W. J. Chem. Phys. 1964, 41, 2297. (b) Battin-Leclerc, F.; Smith, A.P.; Hayman, G.D.; Murrels, T.P. J. Chem. Soc., Faraday Trans. 1996, 92, 3305.