# RECENT FINDINGS ON THE OXIDATION OF $UO_2$ FUEL UNDER NOMINALLY DRY STORAGE CONDITIONS*

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## ABSTRACT

This paper is an overview of fuel-storage demonstration experiments, supporting research on $UO_2$ oxidation, and associated model development, in progress at AECL's Whiteshell Laboratories. The work is being performed to determine the time/temperature limits for safe storage of irradiated CANDU fuel in dry air. The most significant recent experimental finding has been the detection of small quantities of $U_3O_8$, formed over periods of one to several years in a variety of experiments at 150-170°C. Another important finding is the slight suppression of $U_3O_8$ formation in SIMFUEL and other doped $UO_2$ formulations. The development of a nucleation-and-growth model for $U_3O_8$ formation is discussed, along with available activation energy data. These provide a basis for predicting $U_3O_8$ formation rates under dry-storage conditions, and hence optimizing fuel storage strategies.

## 1. INTRODUCTION

Dry air storage in above-ground canisters is an important stage in the management of irradiated CANDU fuel, between water-pool storage and deep underground disposal. In Canada, dry storage facilities are currently in use at Point Lepreau and the decommissioned Douglas Point and Gentilly-1 nuclear generating stations, as well as the Whiteshell and Chalk River laboratories (1).

One of the principal limitations on dry-storage temperatures is the oxidation of $UO_2$ in defected fuel elements, which leads to the formation of high-volume solid phases such as $U_3O_8$ and, if moisture is present, $UO_3 \cdot xH_2O$. The former phase has a 36% higher volume (per unit mass U) than $UO_2$, and can therefore cause swelling and splitting of fuel cladding, along with powdering of the oxide fuel matrix (2,3). This could seriously complicate any subsequent handling of the fuel. Although the hydrated oxidation products, $UO_3 \cdot xH_2O$, have still higher specific volumes than $U_3O_8$, there is some indication that their formation may not cause swelling, because an

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aqueous medium is required for dissolution of the fuel and reprecipitation of the hydrate (4-6).

The two-step oxidation of $UO_2$ to form intermediate phases with fluorite-related structures ($U_3O_7$ and $U_4O_{9+z}$)[**], then $U_3O_8$ (which has a completely different, orthorhombic crystal structure) has received a great deal of experimental attention (7). Nevertheless, there is little information on the rate of formation of $U_3O_8$ at temperatures below 200°C, so the evaluation of fuel performance under dry-storage conditions relies heavily on extrapolation of kinetic data from elevated temperatures (2,8-10)

In this paper, we summarize recent findings on $U_3O_8$ formation in various experiments at temperatures below 200°C. We also discuss the literature on the activation energy for $U_3O_8$ formation, and describe an approach to modelling the kinetics of $U_3O_8$ formation. Our ultimate aim is to develop a model that can provide a conservative estimate of the rate of $U_3O_8$ formation for a given storage scenario. If the margin of conservatism is small (i.e., if our understanding of oxidation is sound and comprehensive), then it should be possible to optimize fuel storage strategies and hence reduce overall storage costs.

## 2. DEMONSTRATION EXPERIMENTS (CEX-1, CEX-2, ACX)

Since 1978, storage of irradiated CANDU fuel in nominally dry air has been evaluated by ongoing demonstration experiments ("Controlled Environment Experiments", CEX-1 and CEX-2). In these experiments, irradiated fuel bundles are stored in sealed containers in contact with dry air (CEX-1) and moisture-saturated air (CEX-2) at 150°C (11-16). Both intact and deliberately defected bundles are included in the experiments. Defected fuel elements are retrieved at intervals of 2-3 years for detailed destructive examination, with attention to the mechanical condition of the cladding as well as the physical and chemical state of the fuel matrix (12,13). Particular attention is paid to the extent of $UO_2$ oxidation and the identity of the oxidation products; important findings have been summarized by Wasywich et al. (14).

Initially, the CEX-1 and CEX-2 experiments were configured such that there was a limited supply of oxygen, relative to the quantity of $UO_2$ in the defected fuel elements. This was due to practical design limits, combined with the large number of defected elements (all but one of the outer-ring elements in each deliberately defected bundle). In contrast, a commercial-scale fuel storage "basket" would be unlikely to contain more than one defected element, therefore sufficient oxygen would be available to oxidize the exposed $UO_2$ entirely to $U_3O_8$.[***]

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[**] Hereafter, we shall refer to this family of phases collectively as $U_3O_7/U_4O_9$.

[***] One Bruce fuel element contains ~510 g of $UO_2$, which requires ~15 L of $O_2$, or ~73 L of air (measured at 22°C) for complete conversion to $U_3O_8$. One Pickering element contains ~710 g of $UO_2$. Commercial 60-bundle CANDU fuel storage baskets (Pt. Lepreau design) contain ~260 L of air; some other current designs are larger.

Analyses of the container atmospheres in both the CEX-1 and CEX-2 experiments during recent examinations have shown that significant oxygen depletion occurred during the typical intervals of a few years between examinations (14-16). Attempts to model the progress of oxidation have indicated that oxygen depletion may have been quite rapid (17); also, oxidation of internal container surfaces and organic impurities contributed to the depletion. Nevertheless, significant differences in oxidation behaviour were observed between the dry and moist environments. Oxidation in CEX-2 (moist air) was more pervasive along grain boundaries than in CEX-1 (dry air), but was limited to a thin surface film on the grains (14). Oxidation in CEX-1 was more limited in its progress along an element from the defect, but produced thick layers (>1 µm) of $U_3O_7/U_4O_9$ on $UO_2$ grains in the defect region. No $U_3O_8$ was detected in either experiment by XRD, after 100 months of operation with CEX-1 and 69 months with CEX-2.

To help simulate commercial fuel-storage conditions more accurately, the CEX-1 experiment was modified in 1989 to increase the volume of air available to the fuel, by opening a fitting (~4 mm i.d.) on the storage container. This made available to the fuel the air content of the concrete canister in which the experiment is conducted. The available volume of air was thus increased from ~0.8 L to ~48 L per defected element. In 1992, a new experiment (the Alternate Controlled Environment Experiment, ACX) was initiated, in which fuel (selected elements from CEX-2) is exposed to moisture-saturated air at 150°C and provision is made to analyze and replenish the air supply at intervals of about 20 days. Fuel from both the modified CEX-1 and ACX experiments has now been retrieved and examined.

In the modified CEX-1 experiment, fuel elements were examined after ~40 months of exposure to the increased air supply (following ~100 months in limited air) at 150°C. For the first time in the storage demonstration program, traces of $U_3O_8$ were detected by X-ray diffraction (XRD). This was detected in two of the four elements retrieved, and in a total of four of the 16 specimens examined by XRD. The largest amount of $U_3O_8$ found was about 1.7 wt.% of the $UO_2$, based on quantitative interpretation of the XRD data by the method of Choi et al. (18). This is just above the XRD detection limit for $U_3O_8$ (~0.5 wt.%), and was insufficient to cause any detectable fuel swelling, based on profilometry and metallographic examination. The XRD sampling procedure tended to favour recovery of material from the outer surfaces of the fuel fragments, so the fraction of fuel converted to $U_3O_8$, even in the most oxidized specimen, was probably much less than 1 wt.%. So far as we are aware, this is the first reported observation of $U_3O_8$ formation (excluding very thin films) by $UO_2$ fuel oxidation at temperatures below 200°C.

In addition to the formation of traces of $U_3O_8$, the fuel specimens from the modified CEX-1 experiment showed much more extensive oxidation to $U_3O_7/U_4O_9$ than previously, consistent with the substantially increased air supply. Averaged over the four elements examined, 93% of the fuel experienced some oxidation, and in most of the oxidized material the grains had been converted entirely to $U_3O_7/U_4O_9$. Some intragranular cracking was observed, mainly near the defects, which may be related to the onset of $U_3O_8$ formation. More details of these fuel examinations will be presented elsewhere (19).

## 3. SUPPORTING CHEMICAL RESEARCH

### 3.1 Unirradiated Fuel Oxidation

Since 1988, the storage-demonstration experiments have been complemented by a small research program on the chemistry of $UO_2$ fuel oxidation in air. Initially, this program focused on the oxidation process with different moisture levels at 200-225°C (4-6); these temperatures were chosen to accelerate the oxidation so that substantial alteration could be detected in a matter of days or weeks, rather than months or years, of exposure. This work demonstrated that $UO_3 \cdot xH_2O$ phases are formed when sufficient moisture is present to provide a medium for dissolution and precipitation. Under saturated conditions, i.e., 100% relative humidity (RH), large crystals of $UO_3 \cdot xH_2O$ can be formed. At RH values between ~40% and 100%, fine-grained $U_3O_8$ and $UO_3 \cdot xH_2O$ corrosion products are produced by reaction in a thin film of adsorbed moisture.

We have also used XRD to detect the early stages of $U_3O_8$ formation on unirradiated $UO_2$ fuel in air at temperatures between 200°C and 316°C (9). This method provides an early indication of $U_3O_8$ formation, preceding visible powder formation in time by a factor of three to ten. Attempts to derive an activation energy for $U_3O_8$ formation from these data were not very successful, however, because data for different degrees of oxidation to $U_3O_8$ yielded different apparent activation energies, ranging from 124 to 139 kJ/mol (see Section 4.1).

### 3.2 Effects of Fission Products: SIMFUEL oxidation

SIMFUEL is a low-radioactivity material that replicates some of the chemical and microstructural features of irradiated fuel (20). We have investigated the air oxidation of SIMFUEL at 250°C, to determine the chemical effects of fission products on the oxidation rate (18). Materials with various simulated burnup levels (up to 8 atom %, or ~80 MWd/kg U) were tested. The oxidation tests were designed to provide insight into reported differences between irradiated CANDU and LWR fuels. For example, defected CANDU fuel elements (~1 atom % burnup) have been reported to suffer major swelling and splitting after ~200 h at 250°C, whereas irradiated LWR fuel fragments (~2-5 atom % burnup) showed no sign of $U_3O_8$ formation after 10,000 h at the same temperature (3,21).

Our experiments indicated that the behaviour of SIMFUEL parallels that of irradiated LWR fuels, in that there is a gradual suppression of $U_3O_8$ formation with increasing burnup (18). This effect is illustrated in Figure 1, which compares the induction period for $U_3O_8$ appearance on SIMFUEL with analogous data reported for irradiated LWR fuels. Qualitatively similar findings have been reported with $UO_2$ specimens containing a single dopant element, such as Gd, indicating that fission products in solid solution in $UO_2$ play an important role in suppressing the nucleation or growth, or both, of $U_3O_8$ (23).

### 3.3 Oxidation of Unirradiated Fuel in a Radiation Field

We are investigating the oxidation of unirradiated $UO_2$ in a gamma-radiation field with various oxygen and moisture levels at 150°C (24). The gamma field is comparable to those associated with irradiated CANDU fuel after 10 to 20 years of cooling. These experiments are performed in conjunction with the ACX experiment, making use of an interstitial space between the four vessels containing ACX fuel (which provide the radiation field). The fuel specimens are isolated in individual glass vials containing selected combinations of air, argon, oxygen and water; each combination is run in triplicate.

Recently, fuel specimens were recovered from this experiment after two years at 150°C (with intermittent cooling during air analysis and replenishment for the ACX experiment; see Section 2). The specimens were characterized by X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM), as well as XRD. X-ray photoelectron spectroscopy is a highly surface-sensitive technique that provides information on the oxidation state of the elements analysed, because their core-electron binding energies vary with oxidation state. In the case of uranium, the U $4f_{7/2}$ peak near 380 eV is especially helpful for this purpose (24, and references therein). The most significant findings are discussed briefly below, and further details are given elsewhere (24).

Fuel exposed to a mixture of argon and 60%-saturated steam showed no evidence of oxidation, even to XPS. The XPS spectrum was attributable almost entirely to the original IV oxidation state of uranium in $UO_2$. This indicates that radiolysis of water vapour alone is insufficient to cause any detectable oxidation of $UO_2$ at 150°C.

Fuel exposed to a mixture of oxygen and 60%-saturated steam acquired a fine-grained corrosion-product layer consisting mainly of $UO_3 \cdot xH_2O$ and soddyite ($(UO_2)_2SiO_4 \cdot 2H_2O$), with traces of $U_3O_8$, as identified by XRD. The soddyite is presumably formed by interaction of the uranium oxides with dissolved silica from the glass vessel. In this case, the XPS spectrum of the surface was attributable almost entirely to the fully oxidized VI state of uranium. The microstructure of the corrosion-product layer resembled those observed in our earlier work on air/steam oxidation at 200-225°C (4-6).

Fuel exposed to dry air formed measurable amounts of $U_3O_8$; quantitative analysis by XRD indicated that the outermost ~2 μm contained 0.6 wt.% $U_3O_8$. Somewhat more $U_3O_8$ was formed in the closed vessels than the open ones. The reasons for this difference are not understood; several possibilities have been discussed elsewhere (24). The formation of $U_3O_8$ after 2 years at 150°C is consistent with the results from the modified CEX-1 experiment, as described in Section 2, and also with earlier predictions based on extrapolation from data obtained with unirradiated fuel at 200°C and above (9). Additional experiments are now in progress to establish the effects of radiation fields on $UO_2$ oxidation at 150°C.

### 3.4 Direct Comparison of Unirradiated and Used Fuels

The long-term oxidation of fuel fragments in dry air at 130°C and 170°C is also being examined. These experiments include irradiated LWR fuel (from H.B. Robinson Unit 2, fuel assembly BO-5) as well as both irradiated and unirradiated CANDU fuel specimens (the former from Pickering "A" Bundle PA13894W, element 4). Fuel specimens are currently being examined after 1 year of oxidation; subsequent examinations are planned after 2 years, 3 years (170°C experiment only) and 5 years (130°C only).

An important result from the current examination is the detection by XRD of minor quantities of $U_3O_8$ on the unirradiated $UO_2$ specimens oxidized at 170°C (nominal temperature; actual mean temperature was 168.2°C). Quantitative analysis of the XRD data indicated 1.0 wt.% $U_3O_8$ within the analysed surface layer (~2 µm). No $U_3O_8$ was detected on the irradiated fuel specimens, but this was possibly due to the sampling procedure, which involved powdering a substantial fraction of the specimen. In contrast, the flat surfaces of the unirradiated fuel specimens could be examined directly.

The extent of $U_3O_7/U_4O_9$ formation for both of the irradiated fuel types at 170°C (based on weight changes) was consistent with published data (8,25). Weight gain by the irradiated fuels was much faster than by the unirradiated fuel, as expected, because of enhanced grain-boundary oxidation (14,25,26).

## 4. MODEL DEVELOPMENT

### 4.1 Activation Energy and Kinetic Model for $U_3O_8$ Formation

Since the pioneering investigation by Aronson et al. (27) in 1957, the sequential oxidation of $UO_2$ to $U_3O_7/U_4O_9$ and $U_3O_8$ has been studied by many researchers, as summarized in a recent review (7). The literature dealing with the activation energy for $U_3O_8$ formation is very confusing. In most cases, no distinction has been made between the activation energies for nucleation versus growth of $U_3O_8$; in some cases, the activation energies is estimated from the overall oxidation rates, i.e., without distinction between $U_3O_7/U_4O_9$ and $U_3O_8$ formation.

The assortment of reported activation energies for $U_3O_8$ formation ranges from 48 to 194 kJ/mol. A critical review of these values is essential before any realistic extrapolation to dry storage temperatures can be made. If we restrict our survey to studies below 300°C that clearly distinguish $U_3O_8$ formation, the range of values is reduced to 124-172 kJ/mol, with an average of 158 kJ/mol (2,9,27-31).

We have recently developed a sensitive, quantitative method of monitoring the formation of $U_3O_8$ on $UO_2$, by applying a quantitative XRD technique (18) to the procedures described by Taylor et al. (9). The extent of $U_3O_8$ formation on the surface of $UO_2$ disks was measured by comparing the integrated intensity of the $U_3O_8$ diffraction peaks with those of a series of calibrated standards. The progress of oxidation was found to follow sigmoidal nucleation-and-growth kinetics, as expected.

The kinetic data have been compared with a two-dimensional model for surface nucleation and growth, which was developed to extract rate constants from the experimental results (32). The model calculates the expected fraction of $U_3O_8$ on the surface of $UO_2$ disks by considering the formation of circular $U_3O_8$ nuclei at a given rate $K_N$ (nuclei/hour) and the subsequent growth of these nuclei at a rate $K_G$ (m/h) on the two-dimensional surface of the $UO_2$ disk. The theoretical method correctly models the sigmoidal reaction kinetics, and yields a combined rate constant $\kappa = K_G^2K_N$. A preliminary Arrhenius plot for $\kappa$ is shown in Figure 2; this plot yields an activation energy of 146 ± 10 kJ/mol for the temperature range 170-300°C. The quoted uncertainty represents the 90% confidence interval. This result may be compared with the range of values from 124 to 139 kJ/mol, obtained previously by semi-quantitative treatment of a smaller data set (9).

## 4.2 A Conservative Mechanistic Model for Dry Storage

We suggest the following approach to developing a conservative model of $U_3O_8$ formation.

(a) Define a maximum acceptable degree of oxidation to $U_3O_8$ in defected fuel elements;

(b) Determine a time-temperature relationship (and estimate the uncertainty limits) for this degree of oxidation to occur with unirradiated fuel;

(c) Provide convincing evidence that unirradiated $UO_2$ represents a conservative case, *or* include an expression to account for fuel burnup;

(d) Take account of any radiation effects.

Hastings et al. (8) have estimated that CANDU fuel can undergo about 15% conversion to $U_3O_8$ before sheath splitting occurs (i.e., up to 15% conversion, the fuel expansion is accommodated by swelling alone). Thus, one possible (very conservative) criterion for the maximum acceptable degree of oxidation might be 1.5% conversion of an exposed fuel surface. This is an order of magnitude lower than the threshold value for sheath splitting, and it also takes no credit for non-uniform oxidation of the fuel (i.e., slower oxidation of internal regions of fuel fragments). The 1.5% conversion criterion is also a degree of oxidation that can be measured by XRD on a flat specimen of unirradiated fuel (and, in principle, on a flat irradiated fuel specimen, although this presents practical difficulties). In other words, this is an experimentally verifiable criterion.

Reports on the air-oxidation behaviour of LWR fuel (21-23) and our own work on SIMFUEL (18), suggest that unirradiated $UO_2$ should represent a conservative case, i.e., there is no evidence that any irradiated fuels are intrinsically more reactive than $UO_2$ with respect to $U_3O_8$ formation.

For modelling purposes, data for $UO_2$ with a rough surface should be used, because highly polished specimens are somewhat more resistant to $U_3O_8$ formation than rough-finished specimens (9,33). This is probably attributable to a higher density of nucleation sites on the rougher surfaces. The use of data for surfaces with a high density of nucleation sites represents further conservatism in our model.

At present, we do not have sufficient information to evaluate radiation effects completely. These may be either direct effects on solid reactivity (i.e., introduction of lattice defects that influence oxidation kinetics) or indirect effects from air/moisture radiolysis (i.e., formation of oxidants that are more reactive than $O_2$).

Using the data discussed in Section 4.1, we have estimated the time required for 1.5% surface conversion of $UO_2$ to $U_3O_8$ at various temperatures. Table 1 shows these estimates, expressed as upper and lower limits of the 90% confidence interval. These values should be regarded as preliminary estimates, although they are reasonably consistent with some of the experimental data obtained at 150°C and 170°C, as discussed in Sections 2, 3.2 and 3.3.

## 5. CONCLUSIONS

Recent experimental results indicate that there is no threshold temperature for $U_3O_8$ formation; it occurs slowly (over a period of years) at temperatures as low as 150°C. It is important to quantify the rate of $U_3O_8$ formation, in order to evaluate various dry-storage scenarios. A critical review of literature data and our own experimental results indicates that the activation energy for $U_3O_8$ formation on unirradiated $UO_2$ is probably within the range 140 to 160 kJ/mol. Work on SIMFUEL and irradiated fuels indicates that they are converted to $U_3O_8$ more slowly (per unit surface area) than unirradiated $UO_2$, although the available surface area for oxidation may be much higher in irradiated fuel. Based on these findings, we propose an approach to a conservative model for evaluating fuel oxidation under dry-storage conditions.

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TABLE 1: ESTIMATED TIMES FOR 1.5% SURFACE CONVERSION (OUTERMOST 2 μm) OF $UO_2$ TO $U_3O_8$ ****

| T (°C) | Lower estimate (90% confidence) | | Upper estimate (90% confidence) | |
|---|---|---|---|---|
| | t (hours) | t (years) | t (hours) | t (years) |
| 100 | $7.2 \times 10^6$ | 820 | $8.8 \times 10^7$ | 10000 |
| 150 | $3.4 \times 10^4$ | 3.8 | $2.7 \times 10^5$ | 31 |
| 170 | $5.4 \times 10^3$ | 0.6 | $3.9 \times 10^4$ | 4.5 |
| 200 | 460 | | 3000 | |
| 250 | 13 | | 83 | |
| 300 | 0.6 | | 5.3 | |

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**** Based on the regression analysis illustrated in Figure 2

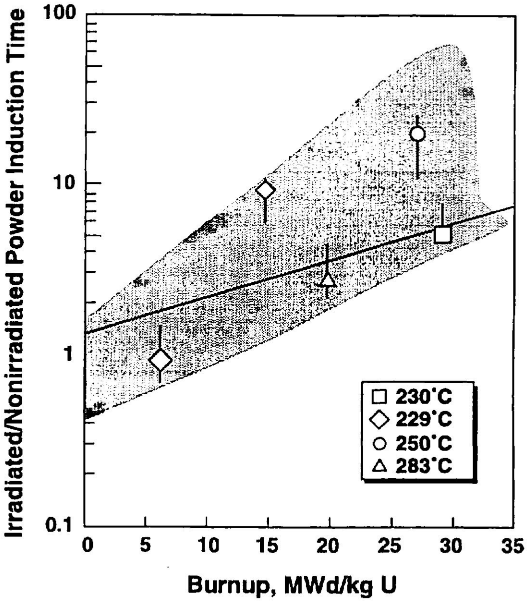

FIGURE 1. RELATIVE INDUCTION TIMES FOR $U_3O_8$ FORMATION ON USED LWR FUELS AND SIMFUEL AS A FUNCTION OF BURNUP, FROM REF. 20. THE SOLID LINE IS A REGRESSION LINE FOR DATA OBTAINED WITH SIMFUEL AT 250°C, SUPERIMPOSED ON USED-FUEL DATA FOR VARIOUS TEMPERATURES FROM REF. 22. THE SHADED AREA REPRESENTS THE RANGE OF UNCERTAINTY FOR THE LWR FUEL DATA.

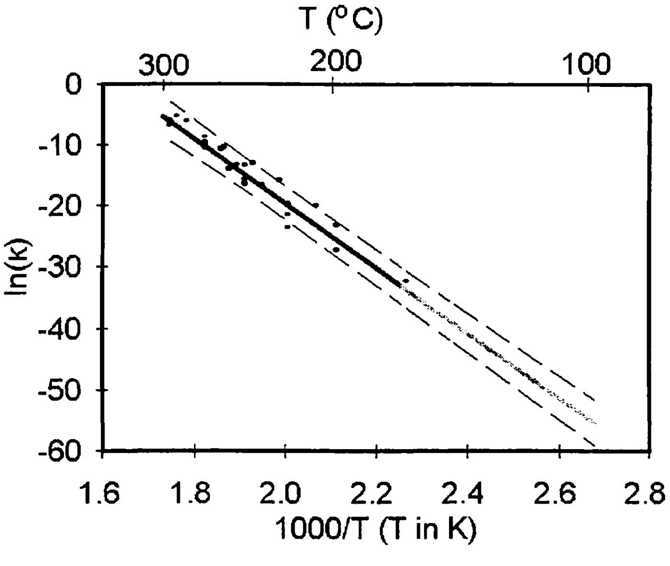

FIGURE 2. ARRHENIUS PLOT OF THE RATE CONSTANT $\kappa$ FOR THE FORMATION OF $U_3O_8$ ON UNIRRADIATED $UO_2$ COUPONS, BASED ON QUANTITATIVE XRD ANALYSIS OF DATA PREVIOUSLY DISCUSSED IN REFERENCE 9, AS WELL AS MORE RECENT DATA. THE SLOPE CORRESPONDS TO AN ACTIVATION ENERGY OF 146 ± 10 kJ/mol (90% CONFIDENCE INTERVAL).