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Kinetics of O₂ depletion in an air-saturated (74.7 ppm O₂) paraffin blend (Exxsol D-80) were conducted with a near-isothermal flowing test rig using passivated heat-exchanger tubing over the range 408–438 K. Hydroperoxide formation was monitored by cyclic voltammetry. Autoxidation data are consistent with an initiation mechanism involving hydroperoxide dissociation; the kinetic data are independent of the initial O₂ concentration. Data analysis yielded the following rate parameters: $\log(k_i/s^{-1}) = (15.2 \pm 1.6) - (33.1 \pm 3.1)/\theta$, $\log[k_{iv}(k_i/2k_v)^{1/2}/M^{-1/2}s^{-1}] = (9.5 \pm 0.2) - (26.3 \pm 0.4)/\theta$, and $\log[(k_{iv}/2k_v)^{1/2}/M^{-1/2}s^{-1/2}] = (3.3 \pm 1.3) - (12.5 \pm 2.6)/\theta$ (where k_i , k_{iv} , and k_v are rate constants for initiation, propagation, and termination, respectively, $\theta = 2.303RT$ kcal mol⁻¹, R is the ideal-gas-law constant, and T is absolute temperature). Results are discussed with reference to kinetic parameters reported for conventional aviation fuels and normal paraffins.

Introduction

Aviation fuels, which are a complex mixture of normal and cyclic paraffins, aromatics, and heteroatomic compounds, may be subjected to severe thermal oxidative stress because of their application as a heat sink in modern aircraft.¹ Surface fouling resulting from this use can be reduced by utilizing highly refined fuels. For example, mild hydrotreatment lowers the concentration of metals and O-, S-, and N-heteroatom-containing species implicated² in reduced thermal stability. More severe hydrotreatment can reduce the total aromatic content.³ Certain high-performance military aircraft such as the SR-71 require specialty JP-7 fuels having low vapor pressure, high thermal oxidative stability, high heats of combustion, and very low concentration of heteroatoms. These requirements can be met by mixing blends of paraffin and cycloparaffin stocks having very low aromatic content and by introducing a lubricity additive.⁴ The commercial solvent blend Exxsol D-80, manufactured by Exxon for use as a reaction diluent, possesses some desirable characteristics as a model fuel. Exxsol D-80 is composed of 58% normal paraffins, 41% cycloparaffins, and 0.8% aromatics; it is equivalent to a JP-7 fuel without a lubricity additive.

It is also representative of severely hydrotreated fuels having reduced aromatic content. Furthermore, since it contains neither synthetic antioxidant nor dissolved metals, it provides an ideal model system for studying autoxidation without added inhibition or metal-catalyzed initiation. These characteristics make Exxsol D-80 an excellent candidate for use as a model for comparison with conventional fuels. In this study, we report the liquid-phase oxidation kinetics measured for air-saturated Exxsol D-80 with the near-isothermal flowing test rig (NIFTR). The data are discussed with reference to those reported for simple hydrocarbons and hydrotreated fuels.

Experimental Section

All experiments were conducted in a single-reaction phase at a system pressure of 2.3 MPa using the NIFTR apparatus that has been described in detail elsewhere.⁵ Reaction occurred as the fuel was pumped slowly through 0.318-cm-o.d., 0.216-cm-i.d. tubing passivated by the Silcosteel⁶ process and clamped tightly within an 81.3-cm heated Cu-block (40 kg) heat exchanger. Stress duration—the residence time within the heated tube—was varied by changing the fuel flow rate and was calculated based on plug flow. Relative dissolved O₂ concentrations of unstressed and stressed fuel were measured using the high-pressure GC sampling method of Rubey.⁷ Calibration based on an independent GC-MS measurement⁸ of 74.7 ppm (w/w) for air-saturated JP-7 yields an equivalent molarity of 1.88×10^{-3} at 298 K.

(1) Edwards, T.; Anderson, S. D.; Pearce, J. A.; Harrison, W. E., III High-Temperature JP Fuels—An Overview. AIAA Paper No. 92-0683, Presented at the AIAA 30th Aerospace Sciences Meeting and Exhibit, Reno, NV, January 6–9, 1992.

(2) Hazlett, R. N. *Thermal Oxidation Stability of Aviation Turbine Fuels*; American Society for Testing and Materials: Philadelphia, PA, 1991.

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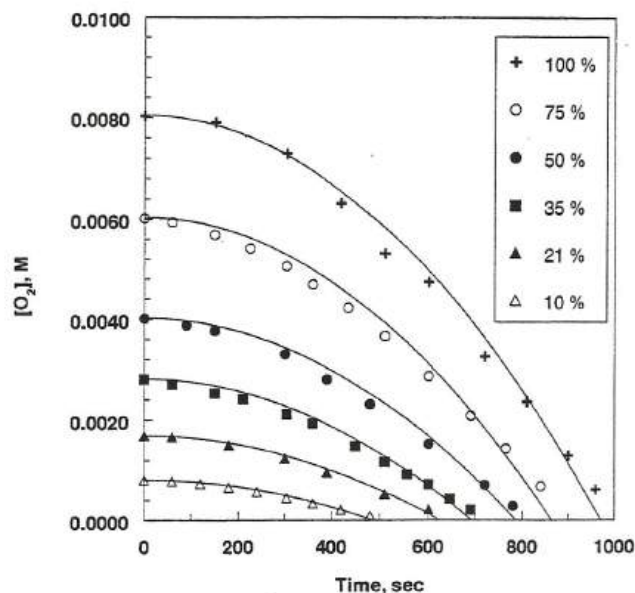


Figure 1. Influence of dilution on O_2 depletion at 413 K (least-squares fit—).

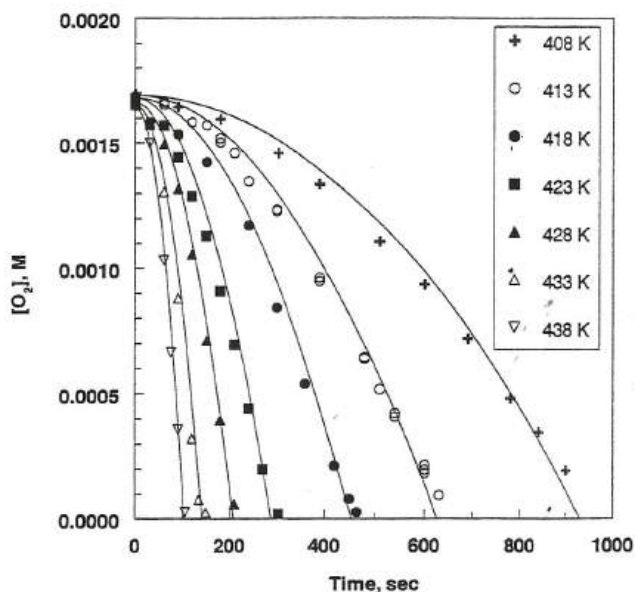


Figure 2. Influence of temperature on O_2 Depletion for air-saturated Exxsol D-80 from 408 to 438 K (least-squares fit—).

Depletion experiments for a 10-fold variation in the initial $[O_2]$ (10–100% O_2 saturation) were conducted at 413 K for assessing the O_2 dependence of the reaction rate. Depletion of O_2 in air-saturated Exxsol D-80 was monitored over the temperature range 408–438 K. Oxygen-depletion data expressed as % O_2 were converted to units of moles per liter (M) from the fuel density within the specified temperature range.

Hydroperoxide formation was monitored from 413 to 433 K using cyclic voltammetry⁹ for samples corresponding to 21% O_2 saturation. Hydroperoxide data were expressed in units of moles per liter (M). Measurements at ambient temperature indicated an initial hydroperoxide concentration of $<10^{-5}$ M.

Results and Discussion

Data. Oxygen depletion versus time plots at 413 K for a 10-fold variation in the initial $[O_2]$ are illustrated in Figure 1. Figure 2 shows the temperature depen-

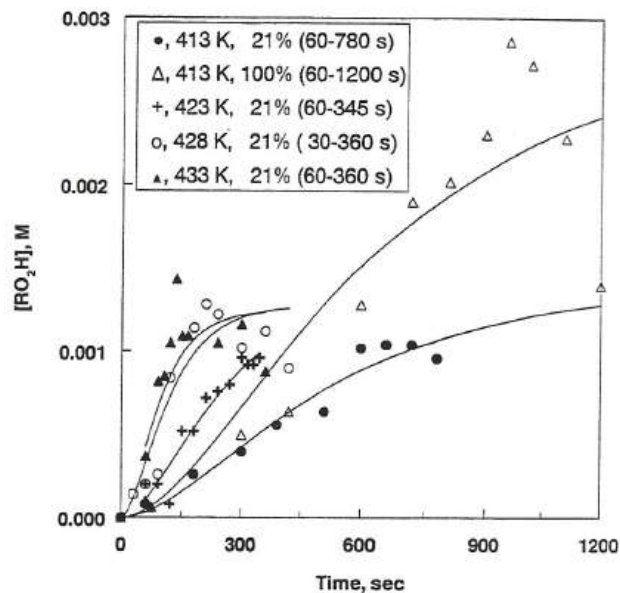
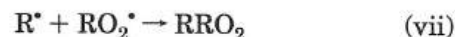
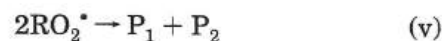
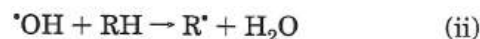


Figure 3. Variation of RO_2H from 413 to 433 K for air-saturated Exxsol D-80 and at 413 K for O_2 -saturated Exxsol D-80. Parenthetical entries are time intervals used for regression (least-squares fit—).

dence for O_2 depletion for air-saturated Exxsol D-80 from 408 to 438 K. Figure 3 demonstrates the change in hydroperoxide content from 413 to 433 K for air-saturated fuel and at 413 K for O_2 -saturated blends, respectively. The O_2 -depletion data given in Figure 1 indicate that initial rates are independent of O_2 ; at longer times, the global rate increases with time.

Reaction Mechanism. The lack of an O_2 dependence for the initial rates, the acceleration at longer time, and the hydroperoxide data are indications that initiation involves trace quantities of hydroperoxide. Thus, the oxidation mechanism may be expressed as



where RO_2H is hydroperoxide, RH is the paraffinic blend, R^* , RO^* , and RO_2^* are alkyl, alkoxy, and peroxy radicals, respectively, and P_1 , P_2 , R_2 , and RRO_2 are molecular products. Reaction i is the major initiation reaction. Reactions iii and iv are propagation steps, and reactions v–vii are termination reactions. Reaction v is the primary termination pathway since $[RO_2^*] > [R^*]$ and $k_{iii} \gg k_{iv}$ at steady state. It is emphasized that each reaction is assumed to be independent of the hydrocarbon chain length and the nature of R^* . Thus, rate

(9) Kauffman, R. E. *Prepr.-Am. Chem. Soc., Div. Pet. Chem.* 1994, 39 (1), 42–46.

constants calculated from experimental data will correspond to global parameters averaged over the total distribution of reactive species.

Application of the steady-state principle to the proposed mechanism yields

$$-\frac{d[\text{O}_2]}{dt} = k_{iv} \left[\frac{k_i}{2k_v} \right]^{1/2} (2[\text{RO}_2\text{H}])^{1/2} [\text{RH}] \quad (1)$$

With the assumptions $[\text{O}_2] = [\text{O}_2]_0(1 - \alpha)$, $[\text{RO}_2\text{H}] = \alpha[\text{O}_2]_0$, $[\text{RH}] = [\text{RH}]_0(1 - \lambda\alpha)$ (where α is the extent of reaction, λ is $[\text{O}_2]_0/[\text{RH}]_0$, and $[\text{O}_2]_0$ and $[\text{RH}]_0$ are initial concentrations), eq 1 may be rearranged to obtain

$$\frac{d\alpha}{dt} = 2^{1/2} k_{iv} \left[\frac{k_i}{2k_v} \right]^{1/2} \frac{[\text{RH}]_0}{[\text{O}_2]_0^{1/2}} \alpha^{1/2} (1 - \lambda\alpha) \quad (2)$$

For hydroperoxide formation, the steady-state hypothesis coupled with the assumption $[\text{RH}] \approx [\text{RH}]_0$ yields

$$\frac{d[\text{RO}_2\text{H}]}{dt} = k_{iv} \left[\frac{k_i}{2k_v} \right]^{1/2} [\text{RH}]_0 [\text{RO}_2\text{H}]^{1/2} - k_i [\text{RO}_2\text{H}] \quad (3)$$

Integration of eqs 2 and 3 yields eqs 4 and 5, where $k_{ap} = k_{iv}(k_i/2k_v)^{1/2}$, $a = 2^{-1/2} k_{iv}(k_i/2k_v)^{1/2} [\text{RH}]_0$, and $b = k_i/2$.

$$[\text{O}_2] = [\text{O}_2]_0 \left[1 - \lambda^{-1} \left(\frac{e^{k_{ap}(2[\text{RH}]_0)^{1/2}t} - 1}{e^{k_{ap}(2[\text{RH}]_0)^{1/2}t} + 1} \right)^2 \right] \quad (4)$$

$$[\text{RO}_2\text{H}] = \left[\frac{a - (a - b)[\text{RO}_2\text{H}]_0^{1/2} e^{-bt}}{b} \right]^2 \quad (5)$$

The $[\text{RH}]$ was calculated for each reaction temperature from the Exxsol D-80 specific gravity (0.8072) and the assumption of an average chain length of 12. Values of k_{ap} were evaluated from nonlinear least-squares fits according to eq 4 using the O_2 -loss data at each temperature given in Figure 2 and a constant value of λ . At 413 K, $[\text{O}_2]_0 = 1.69 \times 10^{-3}$ M and $[\text{RH}]_0 = 3.93$ M, yielding $\lambda = 4.3 \times 10^{-4}$. The $[\text{RO}_2\text{H}]$ data were insensitive to $[\text{RO}_2\text{H}]_0$; therefore, the data in Figure 3 were fitted to eq 5 with the assumption $[\text{RO}_2\text{H}]_0 \approx 10^{-7}$ M. Values for the composite rate coefficients (a and b) were solved simultaneously to obtain values for k_i and $k_{iv}(2k_v)^{1/2}$.

Arrhenius plots are illustrated in Figure 4. A least-squares analysis for $k_{iv}(k_i/2k_v)^{1/2}$, $k_{iv}/(2k_v)^{1/2}$, and k_i yielded eqs 6–8.

$$\log(k_{iv}(k_i/2k_v)^{1/2}/\text{M}^{-1/2} \text{ s}^{-1}) = (9.5 \pm 0.2) - \frac{(26.3 \pm 0.4)}{\theta} \quad (6)$$

$$\log(k_{iv}/(2k_v)^{1/2}/\text{M}^{-1/2} \text{ s}^{-1/2}) = (3.3 \pm 1.3) - \frac{(12.5 \pm 2.6)}{\theta} \quad (7)$$

$$\log(k_i/\text{s}^{-1}) = (15.2 \pm 1.6) - \frac{(33.1 \pm 1.6)}{\theta} \quad (8)$$

Error estimates for the activation parameters in eqs 6–8 are one standard deviation, $\theta = 2.303RT$ kcal mol⁻¹, R is the ideal-gas-law constant, and T is absolute tem-

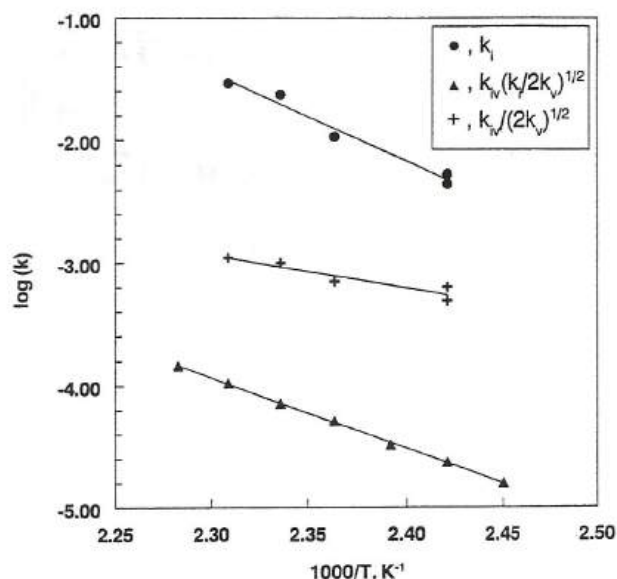


Figure 4. Arrhenius plot for Exxsol D-80 oxidation from 408 to 438 K and RO_2H formation from 413 to 433 K (least-squares fit \rightarrow).

perature. The solid lines in Figures 1 and 2 illustrate the fits obtained from the average rate parameters summarized in eq 6.

Discussion

All of the plots in Figures 1 and 2 exhibit an O_2 dependence that is independent of $[\text{O}_2]_0$ and that accelerates with increasing time. This behavior is expected for autoxidation initiated by trace quantities of hydroperoxide; such behavior is consistent with the observations of Fodor et al.¹⁰ for a series of conventional fuels subjected to thermal stress over the range 316–393 K. The calculated O_2 depletion indicated by the solid lines in Figures 1 and 2 is in excellent agreement with the experimental data. The O_2 -depletion data have a much greater precision than the hydroperoxide data, as evidenced by the standard errors obtained for $k_{iv}(k_i/2k_v)^{1/2}$ and k_i summarized in eqs 6 and 8.

An objective of the present work was to determine whether Exxsol D-80 would be useful as a model for comparison with conventional fuels. If compared with conventional aviation fuels, Exxsol D-80 should closely resemble an additive-free hydrotreated kerosine having a low aromatic content. Fodor et al.¹⁰ reported data for formation of hydroperoxides in a straight-run, additive-free kerosine with an apparent rate constant $\log(k/\text{s}^{-1}) = 10.2\text{--}19.4/\theta$. For Fodor's data, the apparent preexponential factor is expressed as $\log(A_{iv}(A_i/2A_v)^{1/2}[\text{RH}])$. At the average temperature (458 K) for data reported in the present paper, $[\text{RH}] = 3.75$. This may be combined with the preexponential summarized in eq 6 to obtain $\log(A_{iv}(A_i/2A_v)^{1/2}[\text{RH}]) = 10.1 \pm 0.2$, which is in good agreement with Fodor's results¹⁰ for an additive-free kerosine. The associated activation energy for Exxsol D-80 differs from that for the additive-free kerosine by 7 kcal mol⁻¹. The reason for this difference is unknown, but several possibilities exist. The precise nature of the active species in both Exxsol D-80 and the

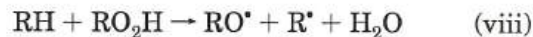
(10) Fodor, G. E.; Naegeli, D. W.; Kohl, K. B. *Energy Fuels* 1988, 2, 729–734.

fuel is unknown—it is probable that only a small fraction in either system is oxidized. For Exxsol D-80, the assumption that the reactive species is solely an aromatic or cycloparaffin would produce a small change in the preexponential factor; the E_{ap} value would remain essentially unchanged. Another possibility is that the fuel contains a species of unknown functionality that renders the component more reactive than a simple hydrocarbon.

Comparative data for the unimolecular dissociation of hydroperoxides are sparse. The benchmark for comparison of the unimolecular dissociation rate constants for RO_2H decomposition is the data of Hiatt and Irwin¹⁴ for *tert*-butyl hydroperoxide with $\log(k/s^{-1}) = (16.1 \pm 1) - (43 \pm 1)/\theta$. The experimental activation energy is close to the value of 42 kcal mol⁻¹ proposed by Benson.¹¹ Several studies^{10,12,13} have shown that the Arrhenius parameters for hydroperoxide homolysis in the condensed phase vary widely. Jensen et al.⁸ utilized a stirred-flow reactor to monitor the autoxidation of *n*-hexadecane; these efforts resulted in $\log(k/s^{-1}) = 8.5 - 26/\theta$. Jimenez and co-workers⁹ obtained $\log(k/s^{-1}) = 11.0 - 30/\theta$ from the autoxidation of *n*-hexadecane, *n*-decane, and *n*-dodecane. Detailed kinetic studies¹⁵ of tetralin hydroperoxide in a series of different solvents yielded activation energies that varied from 18 to 30 kcal mol⁻¹. Disparity between kinetic parameters derived from hydrocarbon autoxidation studies as well as decomposition of the hydroperoxides has been interpreted as an indication of induced decomposition¹⁶ and/or solvent effects.¹⁷ If induced decomposition is the predominant pathway for a particular RO_2H decomposition, this should be manifested in the calculated preexponential factor. For the examples cited,^{10,12-14} the preexponential factors for RO_2H dissociation are within the upper and lower limits expected for bimolecular (11.0) and unimolecular (13.0) reactions. Dissociation of RO_2H formed in the autoxidation of Exxsol D-80 exhibits $\log(A/s^{-1}) = 15.2 \pm 1.6$. This is within the limits for the uncertainty of the preferred value expected for the unimolecular dissociation of *tert*-butyl hydroperoxide. The magnitude of the observed preexponential factor plus the fact that the maximum observed $[RO_2H]$

is always less than 10⁻³ M are strong indications that induced decomposition is not important for the autoxidation of Exxsol D-80.

For Exxsol D-80, $E_i = 33.1 \pm 1.6$ kcal/mol is lower than the value of 42 ± 1 kcal mol⁻¹ proposed by Benson.¹¹ It has been suggested that the activation energy is lower for complications involving solvolysis and induced decomposition. Therefore, it is of interest to comment on the potential for solvent effects upon the rate of initiation. One potentiality¹⁷ may be represented by reaction viii.



It has been suggested that reaction viii would be more energetically favored than reaction i.¹⁷ The assumption of reaction viii as the initiation pathway yields

$$\frac{d\alpha}{dt} = k\alpha^{1/2}(1 - \lambda\alpha)^{3/2} \quad (9)$$

where $k = k_{iv}[k_{viii}/(2k_v)]^{1/2}[RH]_0/(2/\lambda)^{1/2}$. Integration of eq 9 leads to

$$[O_2] = [O_2]_0 \left[1 - \frac{k^2 t^2}{(1 + \lambda k^2 t^2)} \right] \quad (10)$$

Although the functionality of eq 10 differs from that of eq 4, the absolute values of the apparent rate parameters would be essentially unchanged. It should be noted that reaction viii would be accompanied by an increase in translational entropy; this would lead to a larger-than-normal preexponential factor. These observations are consistent with the magnitudes of the Arrhenius parameters determined for $[RO_2H]$ decomposition in Exxsol D-80. However, it should also be noted that reaction viii may, in actuality, be represented simply as the sum of reactions i and ii. Reaction ii would occur with a zero activation energy; hence, the rate-determining step would still be dissociation of the hydroperoxide. These considerations support our initial premise that initiation in Exxsol D-80 involves unimolecular dissociation of RO_2H and is not affected by induced decomposition.

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