

Diester-Base Jet Engine Oils

Here are two possible causes of corrosion in jet engines — acidolysis and hydrolysis

PRELIMINARY studies of lead corrosion in aircraft jet engine bearings suggested that the half ester, 2-ethylhexyl hydrogen sebacate, which can be derived from the major component, bis(2-ethylhexyl) sebacate, of most MIL-L-7808 type lubricating oils (5), might be responsible. (Attempts to distill the half ester at 200° C. resulted in its disproportionation.) This observation, coupled with the fact that some suppliers were adding sebacic acid to the oil to inhibit lead corrosion, prompted a study of the equilibrium constant and the kinetics for the reversible reaction: 2 half ester \rightleftharpoons sebacic acid + diester.

Equilibrium constants for acid-ester interchange have been reported for fatty acids and their esters (7, 3), but not for dibasic acids and their esters.

Experimental

A literature survey (2, 4, 6-8) of synthetic methods for producing the half ester led to adoption of the partial esterification procedure. Because resolution of the reaction mixture poses difficulties, pertinent preparative procedures are included.

A mixture of 1.0 mole of 2-ethyl-1-hexanol, 2.0 moles of sebacic acid, 10 grams of *p*-toluenesulfonic acid monohydrate, and 4 pounds of benzene is refluxed until 17 or 18 ml. of water are collected (theoretical 18.9 ml.). After cooling, most of the unreacted sebacic acid is removed by filtration.

The first-stage extraction of the crude concentrate removes *p*-toluenesulfonic acid and sebacic acids. The concentrate is diluted with 2 pounds of ether and treated with 2% potassium hydroxide. Neutralization is continued with successive portions of the base and gentle swirling until the pH of the effluent reaches 6.0 to 6.5. Above pH 6.0 the *p*-toluenesulfonic and sebacic acids are virtually all reacted. The ethereal solution is acidified with hydrochloric acid to convert any half ester soap to the half ester.

Second-stage extraction of the ethereal solution separates the half ester from the diester. Aqueous potassium hydroxide is introduced dropwise just beneath the surface (to alleviate emulsification difficulties) until the pH of the aqueous

effluent reaches 9.0 to 9.5. The half ester is regenerated and separated from sebacic acid salts as an oil by partial acidification (7) to pH 5.6.

To obtain pure half ester the second-stage extraction and regeneration cycles are repeated three times. The ether solution of the half ester is quickly washed with concentrated hydrochloric acid, then with water, and dried over anhydrous sodium sulfate. Concentration gives a 39.0% yield of half ester, which is further purified by molecular distillation at 80° C. to give a water-white product. No disproportionation occurs at this temperature. The combined recovery of diester is 57.0% based on 2-ethyl-1-hexanol.

Because boiling points and refractive

Properties of Half Ester and Diester

Compound	2-Ethylhexyl Hydrogen Sebacate, C ₁₈ H ₃₄ O ₄	Bis(2-ethylhexyl) Sebacate, C ₂₆ H ₅₀ O ₄
B.P., ° C.		
1 mm. Hg	200	212
8μ Hg	80	95
M.P., ° C.	-14 to -15	-55
Sp. gr., d ₄ ²⁰	0.9592	0.9135
Refractive index, n _D ²⁰	1.4528	1.4501

indices of the half ester and diester are close, neither property is an adequate criterion of purity for these compounds. The spectrum of the half ester is practically indistinguishable from that of an equimolar mixture of acid and diester; the only difference is a shift of acid carbonyl absorption from 5.85 to 5.80 microns in the half ester. Saponification and neutralization equivalents taken together are a better criterion of purity. The former agrees with theory; the latter indicates that the half ester contains less than 1% of diester. The identity of the half ester was confirmed by elemental assays.

For acidolysis studies, purified reactants were degassed and sealed under nitrogen in borosilicate glass tubes. All systems were homogeneous at test temperatures. To follow the course of the reaction, vials were withdrawn at stated intervals, quickly cooled, and analyzed (Table I). Pyrolysis was not a seriously complicating factor, as diester and half ester decomposition was less than 0.6% after 7 days at 200° C. and 0.3% after 26 days at 175° C.

In a simple quantitative method the reaction mixture (16 grams) was diluted with 400 ml. of *n*-pentane and cooled to 0° C. As sebacic acid has a solubility of 0.11% in diester, 1.8% in half ester, but only 0.005% in pentane (20° C.), this dilution procedure separates sebacic acid almost quantitatively from the much more soluble half ester and diester. Precipitated sebacic acid was washed on a tared fritted-glass filter with *n*-pentane, dried, and weighed. The filtrate and washings were concentrated, then titrated with 0.25*N* alcoholic potassium hydroxide to a phenolphthalein end point. The caustic titer represents the amount of half

Table I. Composition of Acidolysis Reaction Mixtures

Time, Days	Moles × 10 ⁴			Total Acid Equiv. × 10 ⁴
	Half ester	Sebacic acid	Diester	
175° C.				
0	Nil	250	250	500
1	56	218	223	492
2	95	205	201	505
4	146	180	176	506
7	188	160	155	502
14	239	135	129	509
21	247	129	125	505
26	252	126	123	504
0	500	Nil	Nil	500
4	365	67	63	499
7	327	88	86	503
14	269	116	115	501
26	253	126	122	505
200° C.				
0	Nil	250	250	500
1	119	192	189	502
2	180	163	159	506
4	208	150	146	508
7	244	131	126	506
0	500	Nil	Nil	500
4	308	101	96	510
7	266	119	116	504

¹ Present address, Miami University, Oxford, Ohio

ester, and the diester is determined by difference. Accuracy was established as within 1% by analyzing known mixtures.

Results and Discussion

Acidolysis Equilibria. In pure acidolysis reactions the total number of equivalents of acid is invariant. The nearly constant acidity of the reaction mixtures (Table I) shows that acidolysis reactions are not seriously complicated by pyrolysis. The random variation in total acidity suggests that the over-all error is about 2%.

Progress of the reversible acidolysis reactions was followed by the changing concentrations of reactants (Table I). Graphical extrapolations show that after 21 days at 175° C. and 9 days at 200° C. the mixtures are within 2% of the same composition; approximately half of the reactants have been consumed. The average (extrapolated) composition of the equilibrium mixtures at 175° and 200° C. is: half ester, 0.508 ± 0.002 mole; sebacic acid, 0.252 ± 0.002 mole; diester, 0.244 ± 0.002 mole.

Within the accuracy of the measurements, the distribution of the molecular species at equilibrium is insensitive to temperature and almost statistical—molar concentrations of sebacic acid and diester are equal and half that of the half ester. For the purely statistical case, the equilibrium constant for formation K_f would equal 4.0. The experimental value is 4.2. This indicates close equivalence in the reactivity of the carboxyl groups involved.

The equilibrium composition of any reaction mixture of the three components can be calculated from their initial concentrations and the equilibrium constant. Expressing the relations in terms of the formation reaction:

A' = moles of sebacic acid, A , initially present

D' = moles of diester, D , initially present

H' = moles of half ester, H , initially present

X = moles of A or D consumed

$2X$ = moles of H formed

$$K_f = 4.0 = \frac{(H' + 2X)^2}{(A' - X)(D' - X)}$$

X (moles A or D consumed) =

$$\frac{4A'D' - H'^2}{4(A' + D' + H')}$$

For the special case where no H is initially present, $X = A'D'/(A' + D')$. If no A or D is initially present, $X = H'/4$.

Kinetics. Initial reaction rates for formation of the half ester were obtained from a chord-area graph of changes in concentration *vs.* time. For one mole of an equimolar mixture of sebacic acid and diester, the initial rate of formation

of the half ester is 0.13 mole per day at 175° C. and 0.36 mole at 200° C. From these data, the activation energy for formation of the half ester was calculated as 17.1 kcal. per mole. Data for formation and disproportionation of the half ester indicate that both reactions advance toward equilibrium at comparable rates at a given temperature.

Initial reaction rates at other temperatures would be technically useful, but this information is difficult to obtain experimentally. Above 225° C., pyrolysis becomes increasingly complicating. Below 175° C. the acidolysis reaction would require months to approach equilibrium. Reaction rates at other temperatures may be estimated by extrapolations of an Arrhenius-type plot. The more extended extrapolations give useful guidance as to the order of magnitude for the reaction rate, even though the numerical values have a large uncertainty. At 250° and 300° C., the reaction proceeds toward equilibrium at 17 and 58% per hour, respectively; at 100° C., at 0.02% (Table II).

Table II. Time for Reaction to Proceed Half Way to Equilibrium Is a Useful Characterization of Reactivity^a

Temp., °C.	Initial Reaction Rate ^b	Half Equilibration Time
25	(0.00001)	(100 years)
100	(0.003)	(5 months)
150	0.04	10 days
175	0.13	3.2 days
200	0.36	1.2 days
250	2	5 hours
300	(7)	(1 hour)

^a All values extrapolated except experimental values at 175° and 200° C. Numbers in parentheses have only qualitative significance. ^b Moles of half ester formed/mole of equimolar mixture of reactants/day.

The time required for the reaction to proceed half way to equilibrium is a useful characterization of reactivity. Experimentally, the half equilibration times are 3.2 and 1.2 days at 175° and 200° C., respectively. As the reciprocal of the time required for half equilibration is proportional to the initial reaction rate, half equilibration times may be estimated for other temperatures (Table II). The uncatalyzed acidolysis reaction is too slow at ordinary storage temperature to account for the formation of appreciable quantities of half ester from the sebacic acid sometimes added to inhibit lead corrosion. At engine operating temperatures, acidolysis reactions are fast enough to influence the composition of the used oil. They can be greatly accelerated by catalysts such as strong acids and Lewis acids.

Acidolysis of the diester is much faster than pyrolysis. At 300° C., the initial rate of formation of half ester from

diester and sebacic acid is 29% per hour, compared with a diester pyrolysis rate of about 1%. When the diester is pyrolyzed, the half ester and sebacic acid as well as the olefin, 2-ethyl-1-hexene, are formed (9). All but the olefin participate in the acidolysis equilibrium $A + D \rightleftharpoons 2H$. As the acidolysis reaction is faster, the proportions of sebacic acid and diester found may differ significantly from those initially resulting from pyrolysis.

Conclusions

The half ester, 2-ethylhexyl hydrogen sebacate, disproportionates reversibly into sebacic acid and the diester, bis(2-ethylhexyl) sebacate, reaching an equilibrium composition containing all three components. The equilibrium constant of the disproportionation reaction is 0.25 and the formation reaction is 4.0. The activation energy for formation of the half ester was calculated as 17.1 kcal. per mole.

Kinetic data show that no appreciable quantity of half ester would be formed in MIL-L-7808 oil by uncatalyzed acidolysis reactions during storage. Because lead corrosion can be correlated with an increase in acidity of the stored oil, the corrosive half ester may have been produced by hydrolysis of the diester rather than by acidolysis. At engine operating temperatures (near 200° C.), acidolysis reactions are sufficiently rapid to affect the composition of diester base oils. At diester pyrolysis temperatures of about 300° C., the much faster acidolysis reaction must alter substantially the concentrations of primary pyrolysis products that can be isolated from the system.

Acknowledgment

The authors acknowledge the cooperation of R. E. Kagarise and R. A. Saunders of this laboratory in measuring and interpreting the infrared spectra.

Literature Cited

- (1) Barkenbus, C., Roswell, C. A., Mitts, A. E., *J. Am. Chem. Soc.* **62**, 1251 (1940).
- (2) Contzen-Crowet, C., *Bull. soc. chim. Belges* **35**, 165-98 (1926).
- (3) Gault, H., Chablay, A., *Compt. rend.* **203**, 729 (1936); **207**, 293 (1938).
- (4) Huber, W. F., Lutton, E. S., *J. Am. Chem. Soc.* **79**, 3919 (1957).
- (5) Military Specification MIL-L-7808C, "Lubricating Oil, Aircraft Gas Turbine Engine, Synthetic Base," Aug. 19, 1955.
- (6) Morgan, G. T., Walton, E., *J. Chem. Soc.* **1936**, p. 903; **1938**, p. 444.
- (7) Ruzicka, L., Stoll, M., *Helv. Chim. Acta* **16**, 495 (1933).
- (8) Soffer, M. D., Strauss, N. S., Trail, M. D., Sherck, K. W., *J. Am. Chem. Soc.* **69**, 1684 (1947).
- (9) Sommers, E. E., Crowell, T. I., *Ibid.*, **77**, 5443 (1955).

RECEIVED for review September 26, 1958
ACCEPTED January 16, 1959