NASA TECHNICAL MEMORANDUM NASA TM-77977

SYNTHESIS OF PYROMELLITIC ACID ESTERS

V. A. Fedorova et al.

NASA-TM-78015 19860012041

Translation of "sintez efirov piromellitovoy kisloty," Visnik l'vovskogo politekhnicheskogo institut (Journal of the L'vov Polytechnic Institute), Vol. 139, 1980, pp. 31-33 (ISSN 0460-0436) (UDC 547.585.26)

Source varies: Visnik L'Vivskogo Politekhnicheskogo Institu

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C. 20546 DECEMBER 1985

STANDARD TITLE PAGE

1. Report No. NASA TM-77977	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle SYNTHESIS OF PYROMELLITIC ACID ESTERS		5. Report Date December 1985
		6. Performing Organization Code
7. Author(s) V. A. Fedorova et al.		8. Performing Organization Report No.
		10. Work Unit No.
9. Performing Organization Name and Address The Corporate Word, Inc. 1102 Arrott Bldg. Pittsburgh, PA 15222		11. Contract or Grant No. NASW-4006
		13. Type of Report and Period Covered Translation
12. Sponsoring Agency Name and Address National Aeronautic and Space Administration Washington, DC 20546		14. Sponsoring Agency Code

15. Supplementary Notes Translation of "sintez efirov piromellitovoy kisloty," Visnik l'vovskogo politekhnicheskogo institut (Journal of the L'vov Polytechnic Institute), Vol. 139, 1980, pp. 31-33 (ISSN 0460-0436) (UDC 547.585.26).

16. Abstract This article studies the ester acids necessary for studying the thermochemical properties of pyromellitic acid (PMK)-based peroxides. It covers obtaining a tetramethyl ester of a PMK. The mechanism of an esterification reaction is discussed, as is the complete esterification of PMK with primary alcohol.

17. Key Words (Selected by Author(s))	18. Distribution Statement Unlimited		
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 6	22. Price

SYNTHESIS OF PYROMELLITIC ACID ESTERS

V. A. Fedorova, V. A. Donchak, A. N. Martynyuk-Lototskaya

When studying the thermochemical properties of pyro- /31*
mellitic acid (PMK)-based peroxides, it was necessary to obtain complete and n-alkyl ester acids for this acid.

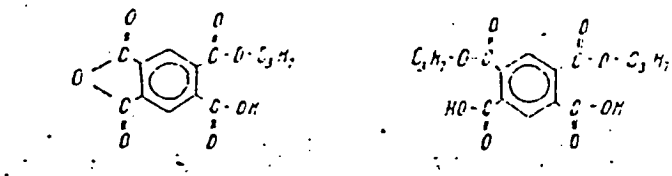
A tetramethyl ester of a PMK is obtained by acylation of alcohols PMK in an air-fluidized bed in the presence of special catalysts [2], in a liquid phase--in the presence of a concentrated sulphuric acid [1] during the interaction of pyromellitic dianhydride (PMDA) with dimethyl sulphite at 110-120°C [3].

The mechanism of an esterification reaction, as it is known, corresponds to the following arrangement: primary protonization of a carboxylic acid for the formation of active particles of electrophilic nature which combines the nucleophilic alcohol with the formation of a secondary oxonium ion. This induces the migration of a proton from alkylated oxygen to hydroxyl with the splitting of a water molecule and the formation of a complex ester. The reactivity of anhydrides is higher than that of carboxylic acids; therefore, the reaction of esterification proceeds with a quantitative yield without the protonization of an anhydride, usually in an excess of alcohol. According to acylating activities, even the acetic anhydride exceeds PMDA. Therefore, the acids of methyl and ether esters were obtained by acylation of suitable alcohols for PMK in a multiple excess of alcohol (usually 20 moles of alcohol for one mole of PMDA) for homogenizing the reaction medium and for completeness of the

---

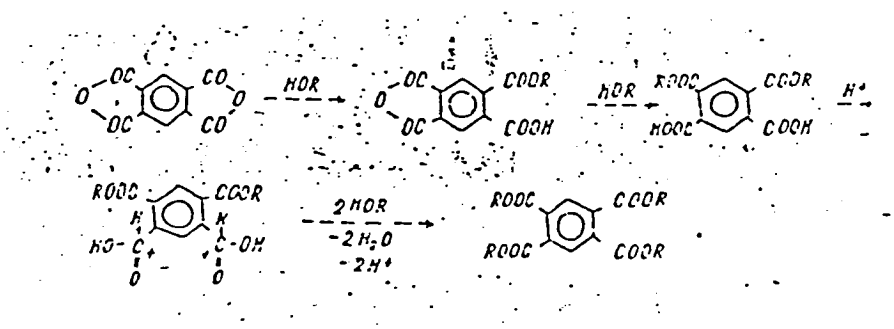
*Numbers in the margin indicate pagination in the foreign text.

acylation reaction at the boiling temperature of a reaction mass. I and II with a yield of 97.8 and 96.7%, respectively, are obtained by using these methods. The acylation reaction rate of n-propyl alcohol is noticeably decreased as a result of the decrease of its nucleophile; therefore, there is a difference in the activity of two reaction centers of PMDA in relation to n-propyl alcohol. For this reason, after an hour's contact with the reagents, a product of half-esterification of IIIa (80%) is obtained and only 20% of an acidic di-n-propyl ester of PMK (III) is as follows



Further esterification of IIIa was reached by an addition to /32 the reaction mass of catalytic quantities of pyridine.

Complete esterification of PMK with primary alcohol prior to the tetraalkyl esters occurs when the reagents are dissolved in concentrated sulphuric acid. The mechanism of this reaction includes two stages: the formation of acids of dialkyl esters of PMK and then the protonization of carboxyl groups which appeared with a nucleophilic substitution for alkoxy groups according to the arrangement



In proportion to the increase of a hydrocarbon radical, a steric hindrance occurs in the alcohol, the reaction rate is reduced, and the product yield is decreased. Thus, IV is obtained by this method with a yield of (97.2%), V--94.4%, and VI--91.7%.

Products I--III are crystallized out by diluting the reaction mass with a 5% solution of HCl. These products (I-III) were purified by recrystallizations from suitable water alcohols and then dried in a vacuum. Tetraalkyl pyromellitic IV-VI were crystallized out when the reaction mass was diluted with ten units of cold water. The precipitated crystals were filtered out and purified by the recrystallizations of water alcohols. Synthesized esters were identified by the boiling temperature or by the melting and element analysis (see table).

Characteristics of di- and tetraalkyl pyromellitic esters

Esters	T°,C	Reaction time, hours	Yield %	Melting temp. (Boiling temp.), °C	Found		Formula	Calculated	
					C, %	K. ch.* mg KOH/g		C, %	K. ch.* mg KOH/g
Dimethyl pyromellitic (I)	66	0,5	97,8	237	51,04	398,0	$C_{12}H_{10}O_8$	51,07	397,6
Diethyl pyromellitic (II)	80	0,5	96,7	219	54,22	361,2	$C_{14}H_{14}O_8$	54,19	361,6
Dipropyl pyromellitic (III)	98	0,5	92,4	142	56,71	333,7	$C_{16}H_{18}O_8$	56,79	334,1
Tetramethyl pyromellitic (IV)	108	2,0	97,2	141	54,12	-	$C_{14}H_{14}O_6$	54,19	-
Tetraethyl pyromellitic (V)	122	2,0	94,4	56	58,98	-	$C_{18}H_{22}O_6$	59,01	-
Tetrapropyl pyromellitic (V)	150	2,0	91,7(242/0,65 millimeters of mercury column)		62,53	-	$C_{22}H_{30}O_6$	62,53	-

*Translator's note: K. ch. may be Curie unit.

It is apparent from the table that by increasing the /33 hydrocarbon radical of an alkoxyl component, a decrease in the melting temperature associated with the increase in the volume of a molecule takes place. Acid esters have a higher melting temperature and are more easily crystallized than tetraalkyl pyromellitic esters.

REFERENCES

1. Nazarov, N. N., Samenovskiy, A. V. "Khlormetilirovania toluola" [Chloromethylation of Toluene], Proceedings from the Academy of Science of the U.S.S.R., Department of Chemical Sciences, 1956, No. 12, pp. 1487-1492.

2. Benning I., Novotny R., Patent 37630 (German Democratic Republic), "Sposob polucheniya efirov karbonovykh kislot" [A Method for Obtaining Esters of Carboxylic Acid], published 07/06/65.

3. Patent 104299 (Holland), "Sposob polycheniya slozhnykh efirov vzaimodeystviem angidridov so spirtami v prisutstvii sernistoy kisloty" [A Method for Obtaining Complex Esters by the Interaction of Anhydrides with Alcohols in the Presence of Sulphurous Acid], published 04/06/63.

The article was received by the editorial staff on May 16, 1979.