[Chem. Pharm. Bull.
27(12)3140—3144(1979)]

UDC 547.584.04 : 542.921.04

Studies on the Thermal Decomposition of Phthalic Acid Esters. IV. Thermal Decomposition of Mono(2-ethylhexyl)phthalate[1,2]

KATSUHIKO SAIDO, SHIGEYASU MOTOHASHI,[3a] TAKESHI KUROKI, TADASHI IKEMURA,[3b]
MASAKICHI SATOMI, and MAKOTO KIRISAWA[3a]

Department of Pharmacy[3a] and Industrial Chemistry,[3b] College of Science and Technology, Nihon University[3]

(Received March 2, 1979)

The thermal behavior of mono(2-ethylhexyl)phthalate (monoester) was investigated in a batch system over the temperature range from 80 to 250°.

After a 12 hr reaction period, around 7% of the monoester was decomposed at 80°. The decomposition reached 50% at 150° and 90% at 250°.

The reaction products were bis(2-ethylhexyl)phthalate (BEHP; 53% at 200°), 2-ethylhexanol and phthalic anhydride. The monoester reacted poorly with water, undergoing hydrolysis only with difficulty. In addition, *cis*-elimination did not occur. The mechanism of the decomposition is discussed.

Keywords——phthalic acid esters; bis(2-ethylhexyl)phthalate; mono(2-ethylhexyl)-phthalate; environmental pollution; thermal decomposition; phthalic anhydride; *cis*-elimination; acyl-oxygen fission

Introduction

Bis(2-ethylhexyl)phthalate (BEHP) is a typical phthalate which is produced in large quantities as a plasticizer for plastics.

Phthalates have caused a number of problems in connection with pollution of both the environment and work places.[4,5] Thus, BEHP is subjected to a variety of heat treatments during the steps of molding, fabrication and waste disposal, and even in a low temperature process such as molding, BEHP undergoes partial decomposition, as indicated by the formation of phthalic anhydride.

The thermal decomposition of BEHP has already been reported on, in part.[6] It was shown that the reaction proceeds through mono(2-ethylhexyl)phthalate (monoester) as an intermediate.[7] This monoester is thought to be toxic, and studies are in progress in the field of hygienic chemistry.[8,9]

Since the monoester is an important intermediate in the decomposition of BEHP, it is necessary to investigate its thermal behavior in order to clarify the behavior of BEHP. However, very little is known about its chemical properties.[10,11]

---

[1] Part III: K. Saido, S. Motohashi, T. Kuroki, d T. Ikemura, M. Satomi, and M. Kirisawa, *Pharm. Bull. Nihon Unive.*, **18**, 11 (1978).

[2] K. Saido, S. Motohashi, M. Satomi, M. Kirisawa, T. Kuroki, and T. Ikemura, Abstr. of Paper Presented at the Pharmaceutical Sect., p. 811, Symposium of College of Science and Technology of Nihon University, Tokyo, Nov., 1977.

[3] Location: *a*), *b*) *101 No. 8, 1-chome, Kanda-Surugadai, Chiyoda-ku, Tokyo.*

[4] F.L. Mayer Jun., D.L. Stalling, and J.L. Johnson, *Nature* (London), **238**, 411 (1972).

[5] K.P. Shea, *Environment*, **14**(9), 11 (1972).

[6] K. Saido, M. Satomi, M. Kirisawa, T. Kuroki, T. Kubo, T. Watabe, and T. Ikemura, *Yakugaku Zasshi*, **97**, 479 (1977).

[7] K. Saido, A. Nakamiya, M. Kirisawa, M. Satomi, T. Kuroki, and T. Ikemura, Abstr. I p. 310 35th National Meeting of the Chemical Society of Japan, Hokkaido, August (1976).

[8] J. Nematollahi, W.L. Guess, and J. Autian, *J. Pharm. Sci.*, **56**(1), 1446 (1967).

[9] P.W. Albro and B. Moore, *J. Chromatog.*, **94**, 209 (1974).

[10] W. Nagel and R.H. Abelsdorff, *Wiss. Veroff. Siemens-Konz.*, **5**, 193 (1926).

[11] G.P. Shulman, J.H. Bennett, and D.G. Botteron, *J. Org. Chem.*, **27**, 3923 (1962).

Thus the monoester was pyrolyzed. Self-catalytic acyl-oxygen fission was found to take place, and the decomposition was not affected by the addition of a small amount of H_2O or alcohol. This paper describes a detailed study on the thermal decomposition of the monoester.

Experimental

Materials——Mono(2-ethylhexyl)phthalate was prepared by reacting equimolar quantities of 2-ethylhexanol and phthalic anhydride at 120° for 10 hr with stirring;[12] white crystals, mp 25—27° (uncorrected). The material thus obtained was treated with an ether solution of diazomethane to furnish methyl 2-ethylhexyl phthalate, which was found to be 99.9% pure by gas chromatography (GC).

Experimental Procedure and Analytical Method——The monoester was heated with certain amount of biphenyl, a heat transfer medium, with stirring under an atmosphere of nitrogen in a three-necked flask equipped with a thermometer, a stirrer and a reflux condenser. The flask and its contents were placed in a silicone bath.

The gas that evolved was cooled with a dry ice-acetone mixture to collect any low-boiling-point components. The reaction mixture was treated with an ether solution of diazomethane to improve the heat stability of the sample, then analyzed by GC, using ethyl benzoate as an internal standard.

A Shimadzu GC-6APF gas chromatograph was used, linked with an ITG-4A integrator. Separation was effected in the following column: Silicone XE-60, 10% on Chromosorb WAW, DMCS, 80—100 mesh, 2 m × 3 mm dia.

The products were identified by various techniques after fractional separation by GC. The instruments used for identifying the components were the same as reported previously.[6]

The decomposition products, identified in their order of elution in the gas chromatogram, were 2-ethylhexanol (EHL), phthalic anhydride (PA), monoester that had not reacted and BEHP. The thermal decomposition of BEHP carried out using a flow system apparatus yielded 2-ethylhexene-1- (EH)[6] as one of the principal components, but this compound was virtually unobserved in the present experiments.

The addition of caprylic acid to the reaction system produced 2-ethylhexyl caprylate (EHC), while the addition of H_2O yielded phthalic acid.

Results and Discussion

The thermal decomposition of BEHP yields the monoester, *via cis*-elimination,[13] which is well known in the thermal decomposition reaction of esters. The formation of the monoester is regarded as the rate-limiting step of the reaction. The present experiment was restricted to the thermal behavior of the monoester in the low temperature range (below 250°).

Effects of Reaction Temperature

Figure 1 shows the effects of reaction temperature on the composition of reaction products on thermal decomposition of the monoester at 80—250° for 12 hours.

BEHP arising from the monoester accounted for 53% of the products at 200°. On the other hand, EHL corresponded to only about 2%.

Figure 1 indicates that the monoester does not undergo *cis*-elimination, which is commonly observed in the thermal decompositions of ordinary esters. The principal reaction is a disproportionation, initiated by intramolecular polarization, yielding EHL and PA. Most of the EHL thus liberated should react with the remaining monoester, affording BEHP. Hence, a rapid decrease in monoester formation appears as an increase in BEHP.

Effect of Reaction Time

Figure 2 shows the effect of the reaction time.

It required 5 minutes for the temperature to reach 150°. The composition was not affected very much by the reaction time, but the amount of PA tended to increase slightly.

---

[12] H. Gilman, "Organic Syntheses," Coll. Vol. I, 2nd, ed. by A.H. Blatt Wiley and Sons, Inc., New York, 1948, p. 418.

[13] C.H. Depuy and R.W. King, *Chem. Rev.*, **60**, 431 (1960).

If the monoester or BEHP being generated should undergo *cis*-elimination, EH would be formed and at the same time the monoester would yield phthalic acid. However, according to the results of our experiments, secondary decomposition of BEHP and *cis*-elimination of the monoester did not take place, and the formation of EH and phthalic acid is negligible.

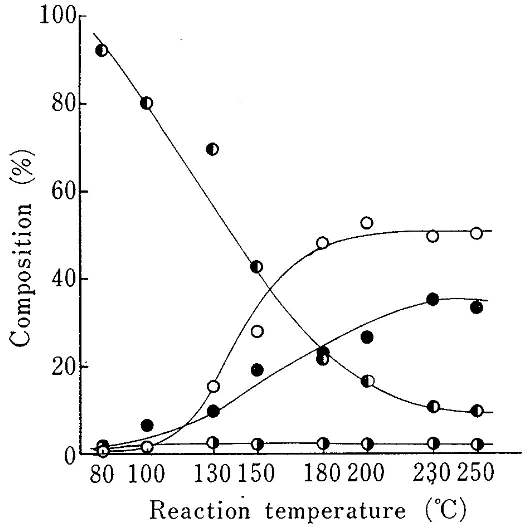


Fig. 1. Effect of Reaction Temperature on the Decomposition of Mono(2-ethylhexyl)phthalate

—◑—: 2-ethylhexanol.
—●—: phthalic anhydride.
—◐—: mono(2-ethylhexyl)phthalate.
—○—: bis(2-ethylhexyl)phthalate.
Reaction time: 12 hr.

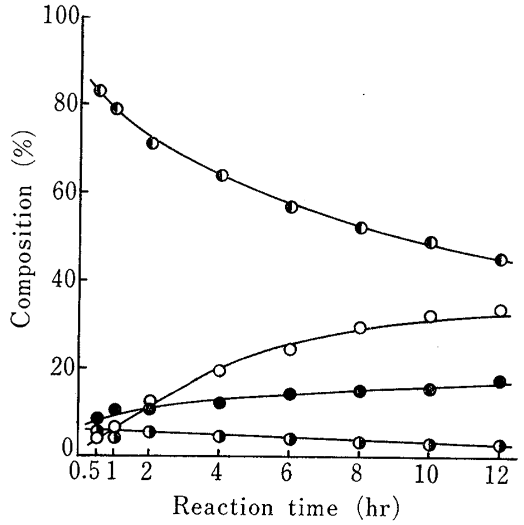


Fig. 2. Effect of Reaction Time on the Decomposition of Mono(2-ethylhexyl)phthalate

—●—: phthalic anhydride.
—◑—: 2-ethylhexanol.
—◐—: mono(2-ethylhexyl)phthalate.
—○—: bis(2-ethylhexyl)phthalate.
Reaction temperature: 150°.

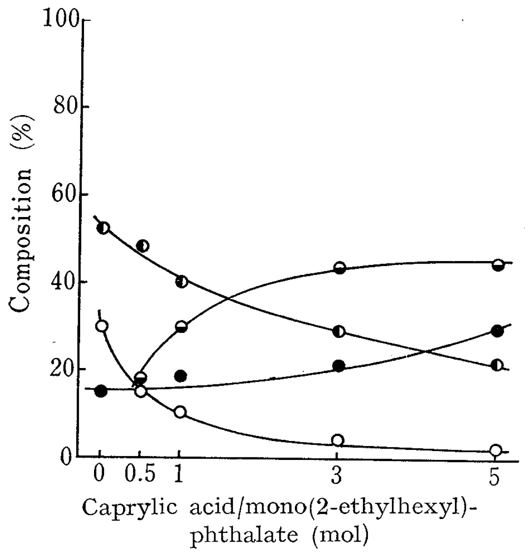


Fig. 3. Effect of Caprylic Acid on the Decomposition of Mono(2-ethylhexyl)phthalate

—●—: phthalic anhydride.
—◒—: 2-ethylhexyl caprylate.
—◐—: mono(2-ethylhexyl)phthalate.
—○—: bis(2-ethylhexyl)phthalate.
Reaction temperature: 150°.
Reaction time: 8 hr.

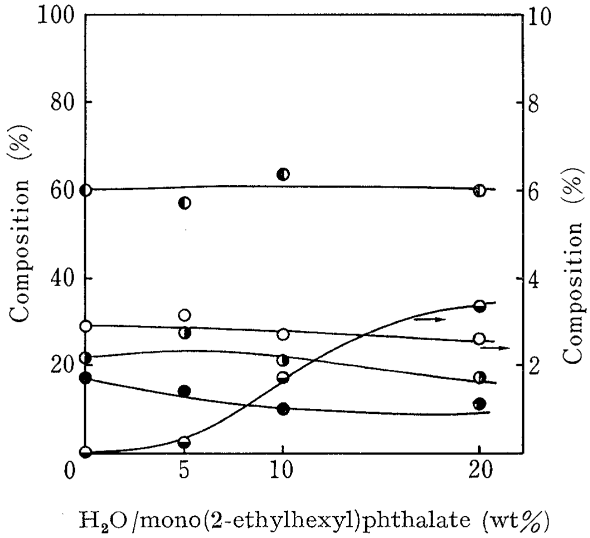


Fig. 4. Effect of H_2O on the Decomposition of Mono(2-ethylhexyl)phthalate

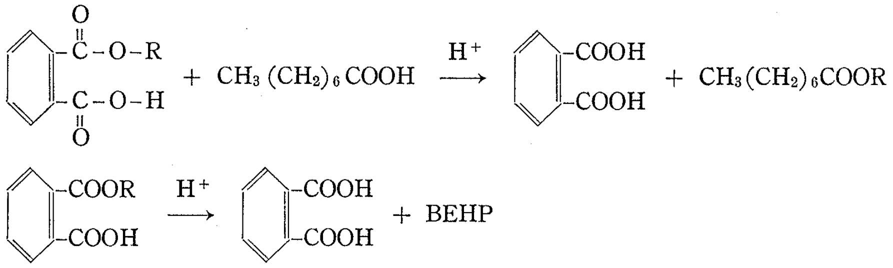
—◑—: 2-ethylhexanol.
—◐—: mono(2-ethylhexyl)phthalate.
—◒—: phthalic acid.
—○—: bis(2-ethylhexyl)phthalate.
—●—: phthalic anhydride.
Reaction temperature: 150°.
Reaction time: 6 hr.

Effect of Acid

Acid hydrolyzes the esters,[14] and may greatly affect the decomposition reaction of the monoester. Thus, the effect of an acid was investigated, and the results are presented in Fig. 3.

As shown in Fig. 3, the amount of monoester decreased as more acid was added. An increase in PA corresponds to decomposition of the monoester. The EHL did not influence the formation of BEHP, but reacted with caprylic acid to give EHC.

Since phthalic acid could not be detected, the following ester exchange reaction did not occur:



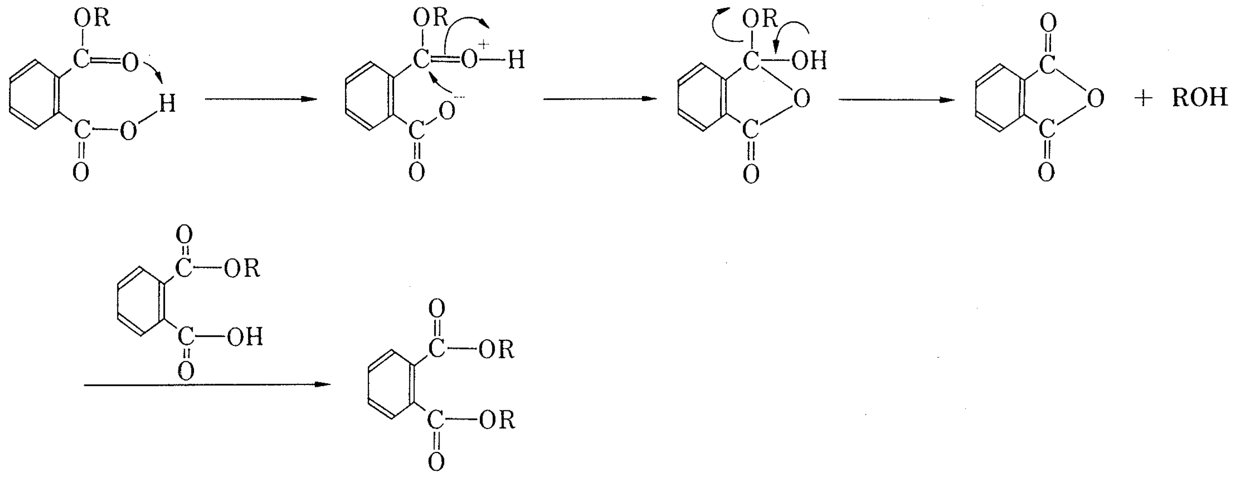
R ; 2-ethylhexyl-

Effect of H_2O

As shown in Fig. 1, BEHP results from an esterification reaction, and this esterification is accompanied by the formation of H_2O. The H_2O thus formed enables the monoester to behave more like an acid and, at the same time, may cause hydrolysis of the monoester. Thus, the effect of H_2O was examined; the results are shown in Fig. 4.

It is clear that an increase in the amount of H_2O does not affect the composition to any appreciable extent. Phthalic acid, an indicator of the occurrence of hydrolysis, begins to form with a 10% addition of water but it is practically absent when there is less than 10%. Therefore, hydrolysis of the monoester does not occur in the presence of low concentrations of H_2O.

However, the monoester is clearly a relatively unstable compound, as shown in Fig. 1. The thermal decomposition of the monoester was presumed to be initiated by intramolecular



R=2-ethylhexyl-

Chart 1

---

[14] G. Davies and D.P. Evans, *J. Chem. Soc.*, **1940**, 339.

proton abstraction by the ester carbonyl from the neighboring carboxylic acid, followed by the attack of the carboxylate anion on the activated carbonyl group as shown in Chart 1.

Conclusions

Mono(2-ethylhexyl)phthalate (monoester) shows considerable thermolability, and the decomposition was a monomolecular reaction. The reaction began at about 80°, and was 50% complete at 150°, and 90% complete at 250°.

The monoester did not undergo hydrolysis or ester exchange reaction, which are commonly observed in the thermal decomposition of ordinary esters. In addition, *cis*-elimination did not occur, though it was observed in the thermal decomposition of BEHP.

The finding that BEHP and PA were produced by thermal decomposition of the monoester suggests that a mechanism involving neighboring group participation operates, as discussed above.

Chem. Pharm. Bull. 27(12)3144—3149(1979)

UDC 547.834.2.02.03 : 543.422.25.06

Stereochemistry of Quinolizidines. VI.[1] Conformation of Benzo[*a*]quinolizidines and Their ^{13}C Chemical Shifts. (2)

Makiko Sugiura, Narao Takao, Kinuko Iwasa,[2a] and Yoshio Sasaki[2b]

Kobe Women's College of Pharmacy[2a] *and Faculty of Pharmaceutical Sciences, Osaka University*[2b]

(Received March 17, 1979)

The conformations of six benzo[*a*]quinolizidine derivatives were studied in terms of the ^{13}C chemical shifts at the C-6 and other positions.

The 9,10,11-trimethoxyl derivatives (IV, V and VI) predominantly adopt the *cis*"a" conformation, whereas I, II and III are predominantly in the *trans* conformation. The equilibrium state "*trans*$\rightleftarrows$*cis*"a"" is discussed in terms of the population of the *trans* conformer, using an empirical approach.

Keywords——^{13}C chemical shift; benzo[*a*]quinolizidine derivatives; conformation; equilibrium state "*trans cis*"a""; population of *trans* conformer;

Introduction

In our previous work,[3,4] we described the correlation between the conformation of benzo[*a*]quinolizidines and their ^{13}C chemical shifts. Benzo[*a*]quinolizidines are well known to have three possible conformations at room temperature, and an equilibrium exists, as illustrated in Chart 1. The ^{13}C chemical shifts of C-6 and C-7 can be used to distinguish these three conformations,[3] and, in particular, the displacement of C-6 chemical shift reflects well the state of the "*trans*$\rightleftarrows$*cis* "a"".[4] Namely, when the *trans* conformation is predominant, C-6 chemical shifts appear in the vicinity of 52 ppm and C-7 in *ca.* 29 ppm. On the

---

[1] Part V: M. Sugiura, N. Takao, H. Fujiwara, and Y. Sasaki, *Chem. Pharm. Bull.* (Tokyo), **26**, 2555 (1978).

[2] Location: *a) Motoyamakita-machi 4-19-1, Higashinada-ku, Kobe 658, Japan; b) Yamadakami 133-1, Suita, Osaka 565, Japan.*

[3] M. Sugiura, N. Takao, K. Iwasa, and Y. Sasaki, *Chem. Pharm. Bull.* (Tokyo), **26**, 1168 (1978).

[4] M. Sugiura, N. Takao, K. Iwasa, and Y. Sasaki, *Chem. Pharm. Bull.* (Tokyo), **26**, 1901 (1978).