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Radiation-Induced Cycloaddition and Polymerization in the Systems N-Ethylmaleimide-Benzene and N-Ethylmaleimide-Isopropylbenzene

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ABSTRACT

The radiolysis of the electron acceptor *N*-ethylmaleimide dissolved in the aromatic donors benzene and isopropylbenzene leads to the 2:1 adduct and to a polymer fraction. The polymer fraction is composed of *N*-ethylmaleimide homopolymer and *N*-ethylmaleimide polymer containing one or two benzene or isopropylbenzene molecules. The ratio of these products depends on the *N*-ethylmaleimide concentration. At low concentration adduct formation predominates, whereas at high concentration homopolymerization of *N*-ethylmaleimide is favored.

INTRODUCTION

Several photochemical reactions between aromatic donors and dienophilic acceptors are described in the literature. Bryce-Smith et al. showed that maleic anhydride and *N*-alkylmaleimides add to benzene and alkylbenzenes [1]. In these cases the photochemical 1,2-cycloaddition is followed by a Diels-Alder addition

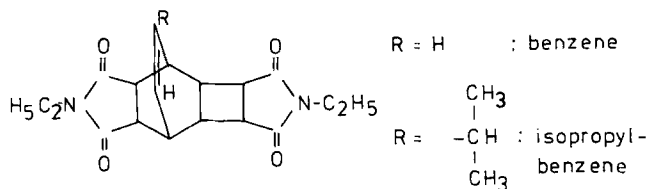
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leading to the 2:1 adduct. In the radiolysis of the system benzene-maleic anhydride, Raciszewski [2] found that, besides an unidentified polymer, the 2:1 adduct is formed. In the system benzene-fumaronitrile, photolysis as well as radiolysis leads to the substitution product phenylsuccinodinitrile [3]. In this paper we want to report on the radiation-induced cycloaddition and polymerization in the systems N-ethylmaleimide-benzene and N-ethylmaleimide-isopropylbenzene.

RESULTS AND DISCUSSION

In the radiolysis of N-ethylmaleimide dissolved in benzene or isopropylbenzene, in addition to radiolytic products of the solvent, the 2:1 adduct (I) and a polymer fraction are produced.



At low concentrations (< 0.1 mole/liter), the 2:1 adduct predominates. The 2:1 adducts were identified by comparing the IR and mass spectra of the radiolytic product with an authentic 2:1 adduct produced by photolysis. The ratio of adduct to polymer was determined by liquid chromatography. The results for different NEMI-concentrations are shown in Table 1.

TABLE 1

C_0 NEMI (mole/liter)	Adduct (%)	Polymer (%)
0.05	90	10
0.2	50	50
1.0	< 3	> 97

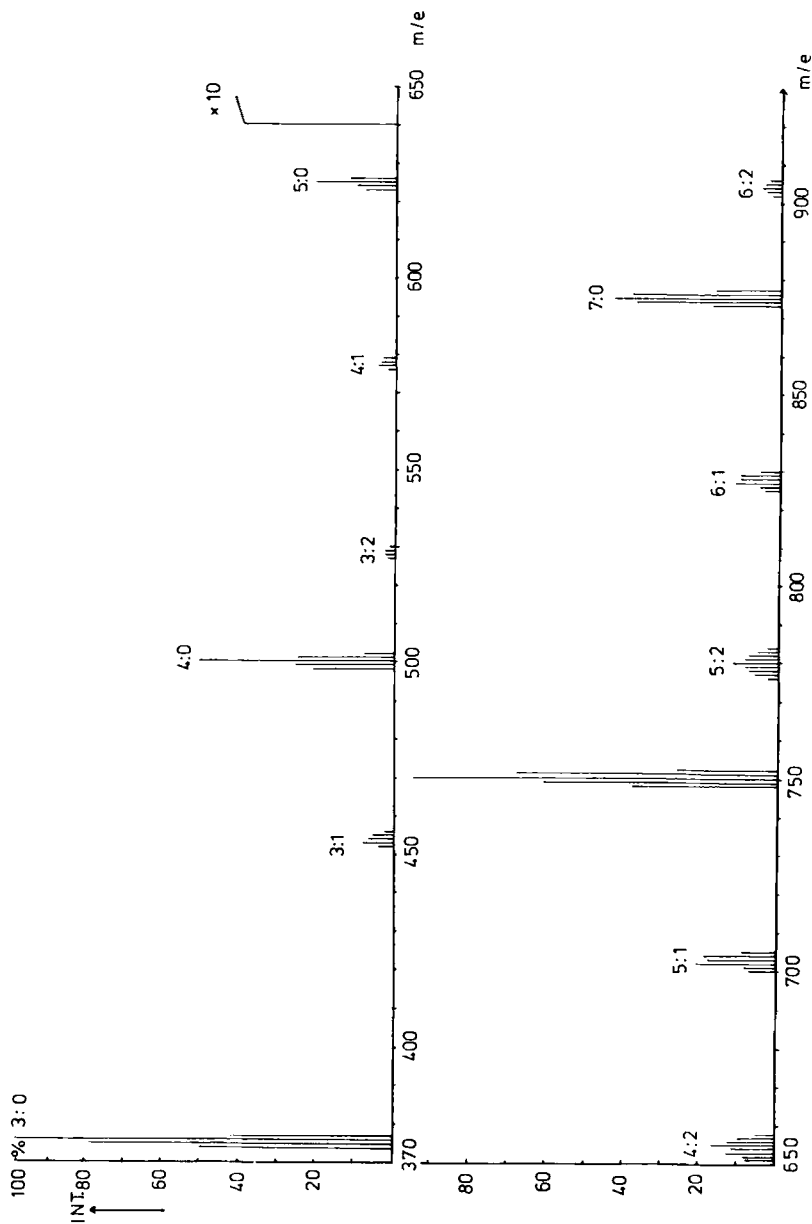


FIG. 1. Excerpt of the mass spectrum of the product at temperature of 573 K in the ion-source (C_0 NEMI = 0.2 mole/liter).

TABLE 2. Intensity Ratio of the Peaks

C_0 NEMI (mole/liter)	$(\text{NEMI})_n : (\text{NEMI})_n (\text{benzene}) : (\text{NEMI})_n (\text{benzene})_2$			
	$n = 4$	$n = 5$	$n = 6$	$n = 7$
0.1	4.5:1:0.8	4:1:0.4	5:1:0.4	5:1:0.3
0.2	9:1:0.4	9:1:0.4	9:1:0.3	9:1:0.3
1.0	8:1:0.9	13:1:0.9	15:1:0.8	20:1:0.8

Information on the structure of the polymer could be obtained by mass spectrometry. At a temperature of 423°K in the ionization chamber for benzene as donor, two additional peak groups with a maximum at m/e 404 and m/e 453 are detected, in addition to the spectrum of the 2:1 adduct. These peaks should correspond to the lowest members of the polymer series: m/e 404, $(\text{NEMI})_2 (\text{benzene})_2$; m/e , 453 $(\text{NEMI})_3 (\text{benzene})_1$. In comparison to the base peak of the 2:1 adduct (m/e 328), the intensity of these peaks is smaller than 0.5%. At a temperature of 573°K in the ion source, the mass spectra depend on the original concentration of NEMI. Figure 1 shows an excerpt of the mass spectrum for C_0 (NEMI) = 0.2 mole/liter.

Peak groups at regular intervals of m/e 125 are observed, which correspond to NEMI homopolymer. Furthermore, peak groups are detected which can be attributed to a NEMI polymer containing one or two benzene molecules. Analogous results were obtained for isopropylbenzene as donor. The spectra give no information to what extent the different peak groups are due to parent ions or to fragment ions of the polymer. With increasing C_0 (NEMI), the intensity of the homopolymer peaks increases in comparison to the peaks of the copolymer. This is shown in Table 2 for benzene as donor.

The initiation of the polymerization of NEMI by an aromatic radical should be responsible for the formation of the NEMI polymer containing one aromatic molecule. A NEMI polymer containing two aromatic molecules should be formed if initiation and termination are due to an aromatic radical.

EXPERIMENTAL

Materials

N-Ethylmaleimide (puriss, Fluka, Ulm) was sublimed twice. Benzene and isopropylbenzene (Uvasol, Merck, Darmstadt) were purified by chemical methods.

Procedure

Radiolysis was performed with radiation from a ^{60}Co source (28,000 Ci) in sealed, degassed glass ampoules at 300°K .

Mass Spectroscopy

Mass spectra of the products were taken on a Varian MAT CH5 spectrometer.

Liquid Chromatography Data

A Hewlett-Packard 1010 B instrument was used with a single column (glass), 50 cm in length, 4 mm, in diameter, filled with $30\ \mu\text{m}$ Alox T. The eluent was dichloromethane; flow rate, 0.5 ml/min; temperature, 300°K .

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