Radiolytic products study of dicyclohexano 18-crown-6-ether, a selective extractant for nuclear fuel reprocessing

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RADIOLYTIC PRODUCTS STUDY OF DICYCLOHEXANO-18-CROWN-6, A SELECTIVE EXTRACTANT FOR NUCLEAR FUEL REPROCESSING

Micheline Draye,[ac] R. Chomel,[a] P. Doutreluingne,[a] A. Guy,[b] J. Foos[b], M. Lemaire*[c]

[a]Service Laboratoire COGEMA, établissement de Marcoule, BP 170, 30205 Bagnols sur Cèze Cédex, France

[b]Laboratoire de Chimie Organique et Département des Sciences Nucléaires du CNAM, 292 rue Saint Martin, 75141 Paris Cédex 03, France

[c]Laboratoire de Catalyse et Synthèse Organique, U.P. 5401, UCBL, Bât 308, ESCIL, 43, bd. du 11 Novembre 1918, 69622 Villeurbanne Cédex, France

The radiolytic products of the DCH18C6 obtained after γ-irradiation have been determined, and the seven main structures have been separated and analyzed. The radiolytic product yields range from about 0.01 to nearly 0.3 molecules per 100 eV absorbed by the DCH18C6 at an energy of 3290 kGy. From the viewpoint of radiation decomposition rate, the DCH18C6 presents a considerable resistance and its radiolytic products have little or no extraction power.

INTRODUCTION

Complexing properties of the DCH18C6 and its applications in various fields of chemistry have been widely

*To whom all correspondence should be addressed.

studied. Thus, the possibility of strontium or plutonium separation from medium and high activity used nuclear fuel and the extraction of radioactive strontium contained in water by the DCH18C6 has been demonstrated[1-3].

In addition, the considerable radiation resistance of solid DCH18C6 has been shown[4,5] and the modifications observed after exposure to γ-irradiation of DCH18C6 chloroform solution have been attributed to the chloroform radiolytic products[5]. However, there is still no definite information on the behavior of DCH18C6 under the action of ionizing radiation and no information on the nature of its radiolytic products.

The present work is concerned with the study of the structural determination of radiolytic products on DCH18C6 γ-irradiation. For each compound, we have reported the number of molecules formed per 100 eV of energy absorbed by the DCH18C6, i.e. the "G" values.

EXPERIMENTAL

The DCH18C6 cis-syn-cis isomer was separated from its other isomer by the method described previously[6].

The samples were made up of 0.2 g of cis-syn-cis DCH18C6 and 2 ml of uranyl nitrate (20 g $U.l^{-1}$) aqueous solution in 1N nitric acid. They were irradiated with a ^{137}Cs γ-source in corked glass flasks. The absorbed energy was, after calibration, 3290 kGy at a dose rate of 19.6 $kGy.h^{-1}$.

After irradiation, to each sample were added 2 ml of CH_2Cl_2 and 20 ml of distilled water. The aqueous phase was extracted with 3 portions of 25 ml CH_2Cl_2.

NMR experiments were carried out on a Bruker AC 200 spectrometer operating at 200.132 MHz (^1H) and 50.323

MHz (^{13}C) under broadband proton decoupling; trifluoroacetic acid was introduced to identify OH functions.

FTIR spectra were recorded on a 1720-X Perkin Elmer spectrometer.

The radiolysis products were separated on a Delsi DI 700 chromatograph equipped with a spiral FJ 1592 non-polar capillary column (25 m x 0.22 mm i.d.) coated with 100% of dimethylsiloxane stationary phase, and they were analyzed on a mass spectrometer Nermag R 10-10H at 70 eV. Two methods of ionization, viz. electron impact and chemical positive ionization with NH_3 were used.

RESULTS AND DISCUSSION

The FTIR results are given in Table 1.

The presence of ether and alcohol functions was confirmed by NMR, but no carbonyl function was identified.

Using gas chromatography, seven radiolytic products and the DCH18C6 were separated and analyzed by mass spectrometry; the characteristic masses obtained are summarized in Table 2.

Masses were identified by chemical ionization. The structures were distinguished by fragmentation analysis using electron impact. For example, compounds B and C, although having the same mass, differ in their structure: with the electron impact, the ion I is characteristic of the structure B and the ion J is characteristic of the other structure C (see Table 3).

The radiolytic product structures of dicyclohexano-18-crown-6 are given in Table 4.

Structures A and C turned out to be the principal products of DCH18C6 radiolysis when the energy absorbed by the crown ether is 3290 kGy.

TABLE 1

FTIR data of dicyclohexano-18-crown-6 and its radiolytic product mixture

Frequency, cm^{-1}	Corresponding vibration
3402	νOH bonded
2937	νas CH_2
2867	νs CH_2
1734	νs C very weak ‖ O
1450	νs CH_2
1099	νs CH_2-O-CH_2
736	ρCH_2

ν = stretching, ρ = rocking, a = asymmetric, s = symmetric.

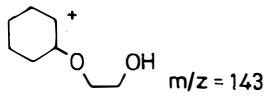
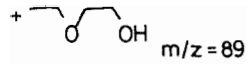
TABLE 2

Chemical ionization mass spectral data for radiolytic products of dicyclohexano-18-crown-6

Compound	M+1	M+18	Corresponding molecule composition
A	161	178	$C_8O_3H_{16}$
B	205	212	$C_{10}O_8H_{20}$
C	205	212	$C_{10}O_8H_{20}$
D	249	266	$C_{12}O_5H_{24}$
E	293	310	$C_{14}O_6H_{28}$
F	303	320	$C_{16}O_5H_{30}$
H	347	364	$C_{18}O_6H_{34}$
DCH18C6	373	390	$C_{20}O_6H_{36}$

TABLE 3

Characteristic fragments of structures B and C

Ion I	Ion J
 m/z = 143	 m/z = 89

The values of the radiochemical yields, G, are listed in Table 5.

The sum of G values corresponding to the seven main products is 0.75. For the number of DCH18C6 molecules disappeared for 100 eV absorbed, we found a value of 0.72 which is comparable to 0.75. Thus, if this macrocycle has to be used in radioactive medium, the molecular structures described in Table 3 could be considered as impurities produced during the process. No radiolytic products have a macrocyclic structure, and the dramatically lower complexing and extracting properties of open chain polyethers compared to the macrocyclic "analogs" has been demonstrated[7]. For example, the complexation of the K^+ and Ba^{2+} by the 18-crown-6 is, respectively, 9,000 and 55,000 times as high as with the pentaglyme.

DCH18C6 possesses high stability towards radiolysis: the power of the dose received during our experiments (3290 kGy) is 11 times as high as the one estimated during a reprocessing campaign, but nevertheless 50% of DCH18C6 remains unchanged.

TABLE 4

Radiolysis product structures of dicyclohexano-18-crown-6

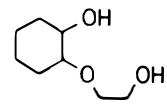
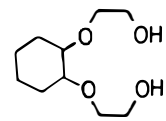
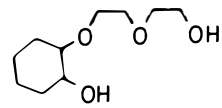
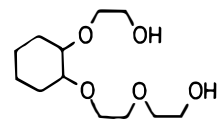
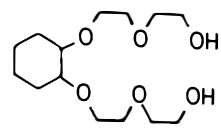
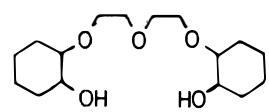
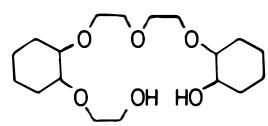
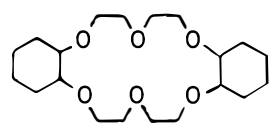
Compound	m/z	Corresponding molecule composition
A	160	
B	204	
C	204	
D	248	
E	292	
F	302	
H	346	
DCH18C6	372	

TABLE 5

Product yields from the radiolysis of dicyclohexano-18-crown-6, molecules/100eV

Compound	Molecules/100 eV
A	0.29
B	0.04
C	0.23
D	0.06
E	0.03
F	0.01
H	0.09
A+B+C+D+E+F+H	$\Sigma G = 0.75$

On the other hand, its radiolytic products give rise to molecules exhibiting very poor extracting properties contrary to that demonstrated for TBP[8].

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