LÜHITEATEID * КРАТКИЕ СООБЩЕНИЯ

https://doi.org/10.3176/chem.1980.4.12

EESTI NSV TEADUSTE AKADEEMIA TOIMETISED. 29. KÖIDE
KEEMIA. 1980, NR. 4

ИЗВЕСТИЯ АКАДЕМИИ НАУК ЭСТОНСКОЙ ССР. ТОМ 29
ХИМИЯ. 1980, № 4

УДК 547.7 : 542.943.5 : 541.141.8

*M. GUBERGRITS, Lia PAALME, Helvi UIBOPUU, J. PAHAPILL,
Odette PERIN-ROUSSEL, F. PERIN, P. JACQUIGNON*

ABOUT THE INITIATED OXIDATION OF SOME DIBENZOCARBAZOLES

M. GUBERGRITS, Lia PAALME, Helvi UIBOPUU, J. PAHAPILL, Odette PERIN-ROUSSEL, F. PERIN, P. JACQUIGNON. MÕNEDE DIBENSOKARBASOOLIDE INITSIEERITUD OKSÜDEERIMISEST

М. ГУБЕРГРИЦ, Лиа ПААЛМЕ, Хельви УЙБОПУУ, Ю. ПАХАПИЛЛЬ, Одетт ПЕРЭН-РУССЕЛЬ, Ф. ПЕРЭН, П. ЖАКИНЬОН. ОБ ИНИЦИИРОВАННОМ ОКИСЛЕНИИ НЕКОТОРЫХ ДИБЕНЗОКАРБАЗОЛОВ

Recently we have presented some notes [1, 2] on the relative rate values of fluoranthenes and dibenzopyrenes in UV- and γ-irradiation initiated oxidation reactions. The dibenzopyrenes are stated to be more reactive as compared with the nonalternant hydrocarbons — fluoranthenes in both reaction series (UV- and γ-irradiation).

In this report we present some preliminary results of a kinetic investigation on the oxidative degradation of some dibenzocarbazoles (Table 1, Fig. 1) also initiated by UV- and γ-radiation. The dibenzocarbazoles like PAH studied earlier, may have a physiological activity, and from this point of view the study of degradation of them may be of interest.

The dibenzocarbazoles investigated are synthesized by authors in Gif-sur-Yvette. The kinetics of photo- and γ-initiated oxidative degradation as well the values of lowest excited singlet state energies and

Table 1

Relative rate constants of UV- and γ-irradiation initiated oxidation of dibenzocarbazoles and the values of their E_{S_1}

Substance	k/k_0		E_{S_1}, cm^{-1}	Carc. activity
	UV	γ		
1. Dibenzo(a,i)carbazole	3.85*	4.56*	27 730	+
2. Dibenzo(c,g)carbazole	0.80	0.62	27 460	+++
3. Dibenzo(a,g)carbazole	2.10	0.89*	27 550	++
4. 2-methoxy-dibenzo(c,g)-carbazole	0.88*	0.40	26 300±150	?
5. 2-acetoxy-dibenzo(c,g)-carbazole	4.25	0.51**	26 700±150	?
6. Carbazole	0.70	0.33	29 670	–

* Till 50% decomposition degree, the pseudo-zeroeth-order k is calculated.
** Radiolysed in benzene, all the others in octane.
E_{S_1} — determined in octane.

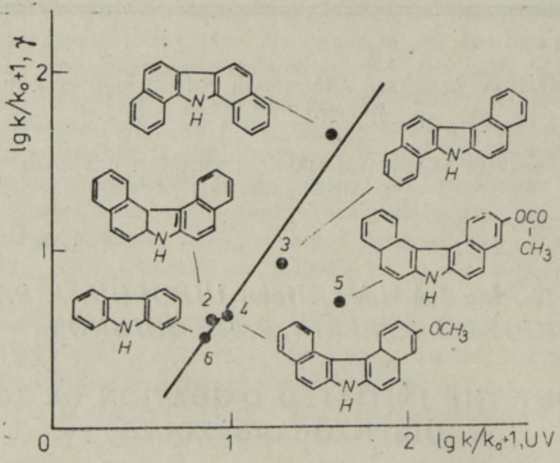

Fig. 1. Comparison of decomposition relative rate constants of UV- and γ-radiation initiated oxidation reactions

UV-spectra have been determined in Tallinn. UV-spectra of carbazoles in ethanol have been registered on the spectrophotometer UV-VIS Specord (Table 2). The mercury-quartz lamps SVD-120 A (intensity 10^{16} quant/cm^{3}sec) were used as the UV-irradiation source, the capacity of γ-^{60}Co-radiation source being about 140 rad/sec. The decomposition was carried out in benzene or octane $2\cdot10^{-4}$ molar solution at 25±1 °C. The variation of the concentration of initial substances during the reaction was checked by spectrophotometric analysis of samples.

The rate constants both of photo-decomposition and of γ-radiation initiated oxidation were calculated from the decrease of the concentration according to the pseudo-zeroeth or the first order reaction (Fig. 2). In order to eliminate the influence of inevitable fluctuations of radiation intensity in various runs, all the kinetic determinations were parallelled with a corresponding experiment with benzo(a)pyrene. The rate constant of the decomposition of dibenzocarbazole (k) was then divided by the rate constant of the decomposition of benzo(a)pyrene (k_0) in the same run. The relative rate constants k/k_0 are listed in Table 1. The k/k_0 values

Table 2

Ultraviolet spectra (experimental) for compounds 1, 2, 3, 4 and 5 (in ethanol)

1		2		3		4		5	
λ, nm	lg ε	λ, nm	lg ε	λ, nm	lg ε	λ, nm	lg ε	λ, nm	lg ε
224.8	4.54	222.0	4.73	221.2	4.69	222.8	4.77	222.8	4.70
258.3	4.47	239.9	4.54	276.3	4.59	255.1	4.40	240.8	4.51
288.7	4.87	254.6	4.33	247.0	4.52	279.6	4.48	280.9	4.51
321.3	4.22	279.0	4.56	265.4	4.58	304.9	4.28	302.7	4.35
335.1	4.17	300.5	4.40	290.7	4.85	352.1	4.18	351.1	4.22
349.2	4.01	333.3	3.92	301.9	4.80	368.7	4.29	368.7	4.38
		349.2	4.28	339.7	4.34				
		366.6	4.46	349.2	4.39				
				366.6	4.17				

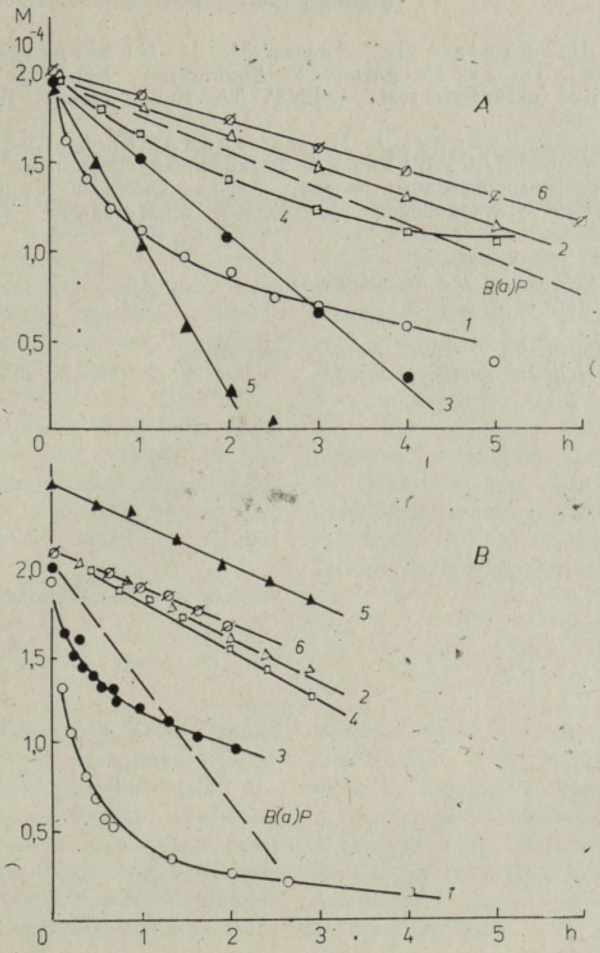

Fig. 2. Kinetics of decomposition of dibenzocarbazoles in UV- (*A*) and γ-radiation (*B*) initiated oxidation reactions (for numeration see Table 1).

for both reaction series (UV- and γ-initiated) oxidation can be well compared with each other, except 2-acetoxydibenzo(c, g)carbazole (5), which, at light-initiated decomposition, oxidizes rapidly and falls outside this correlation (Fig. 1). As seen from Fig. 1, the methoxy- and acetoxy-substitution in the molecule of dibenzo(c, g)carbazole increases its reactivity.

We have also determined the k/k_0 for fluorene, a compound of a structure similar to carbazole, but without the nitrogen atom in the molecule, the values of which are 19.0 in the case of UV-initiation (almost 30 times higher than for carbazole) and 0.44 for γ-initiated oxidation.

A correlation between the values of $\lg k/k_0$ and E_{S_1} of carbazoles studied was not observed.

A more detailed study and discussion on the mechanisms of the oxidative degradation of these compounds in the reactions initiated by UV- and γ-radiation will be a subject of a further study.

REFERENCES

1. Uibopuu, H., Paalme, L., Pahapill, J., Gubergrits, M., Perin-Roussel, O., Jacquignon, P. Fluoranteeni benso- ja naftoderivaatide initsieeritud oksüdeerimisest. — ENSV TA Toim., Keemia, 1979, k. 28, N 2, lk. 131—133.
2. Паальме Л. П., Уйбопуу Х. М., Пахапилль Ю. А., Губергриц М. Я., Жакиньон П. С., Бахна Л. Реакционная способность и молекулярная структура бензпроизводных пирена. — В кн.: Окисление канцерогенных полициклических углеводородов производных бенз(а)пирена. Таллин, 1978, с. 50—56.

Academy of Sciences of the Estonian SSR,
Institute of Chemistry

Institute of Chemistry of CNRS Natural Substances
(Gif-sur-Yvette, France)

Received
April 18, 1980