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OXIDATION OF CARBAZOLE BY HYDROGEN PEROXIDE

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Aarne БОГДАНОВ. ОКИСЛЕНИЕ КАРБАЗОЛА ПЕРЕКИСЬЮ ВОДОРОДА

The elucidation of the role of chemical carcinogens in the aetiology of cancer has received much attention in recent decades. Part of the efforts have been directed to the role which could be played by polycyclic heterocyclic hydrocarbons (PHH), resulting in an increasing number of biological and chemical studies involving these compounds. Such research results in the production of wastes contaminated with PHH and the handling of these products involves the risk of contaminating work rooms and laboratory equipment. For these reasons the author investigated chemical degradation techniques which could be applied in such situations.

The investigation of literature indicates that chemical degradation of carcinogenic N-containing five-cyclic hydrocarbons (e.g. dibenzocarbazoles and dibenzacridines) has not received much attention and only a few references could be found [1–4]. On the other hand, it seems interesting that Monsen et al. [5] showed degradation of phenol to carbon dioxide and water when hydrogen peroxide was used. Our aim was to elucidate the usefulness of this degradation technique or its analogs for the destruction of carcinogenic dibenzacridines and dibenzocarbazoles to non-carcinogenic products, which to our knowledge has never been studied. Here we describe the oxidation of carbazole that is a simple and cheap non-carcinogenic model compound for dibenzocarbazoles.

Experimental

Degradation of carbazole. The degradation of carbazole was investigated using treatment by hydrogen peroxide alone and in the presence of manganese(II) chloride or iron(II) sulphate. Experiments were carried out with carbazole (technical grade) purified from ethanol-water (1 : 1) by recrystallization, mp. 245 °C, in the concentration range of its water solubility [6], at 25 ± 1 °C. 5 ml of hydrogen peroxide solution (30%) was added to 50 ml of carbazole solution with magnetic stirring. The concentration of carbazole was measured with spectrophotometer "SPECORD M 40". When needed, 1 ml 0.1 M solution of manganese(II) chloride or iron(II) sulphate was added. The samples were collected at fixed intervals and extracted with 10 ml *n*-hexane (analytical grade). The concentration was determined spectrophotometrically. After that, experiments were repeated 2 to 4 times.

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Results and Discussion

The kinetics of carbazole oxidation using hydrogen peroxide is depicted in Figs. 1—3. The process of the conversion of carbazole up to 60—80% in the presence of manganese or iron salts is described by second-order formal-kinetic equations. As the results show (Table), the addition of manganese(II) chloride or iron(II) sulphate to the degradation medium accelerates the process of carbazole destruction; the most effective is the combination of hydrogen peroxide with iron(II) sulphate.

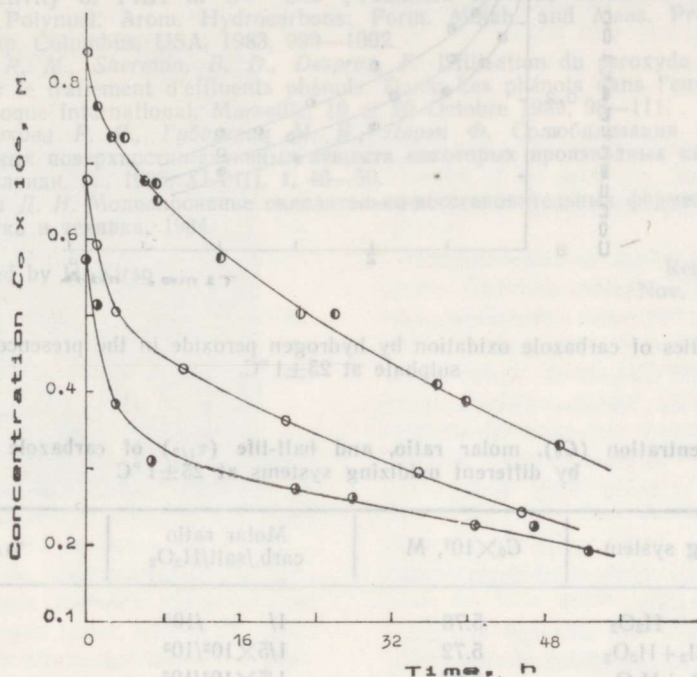


Fig. 1. Kinetics of carbazole oxidation by hydrogen peroxide at $25\pm 1^\circ\text{C}$.

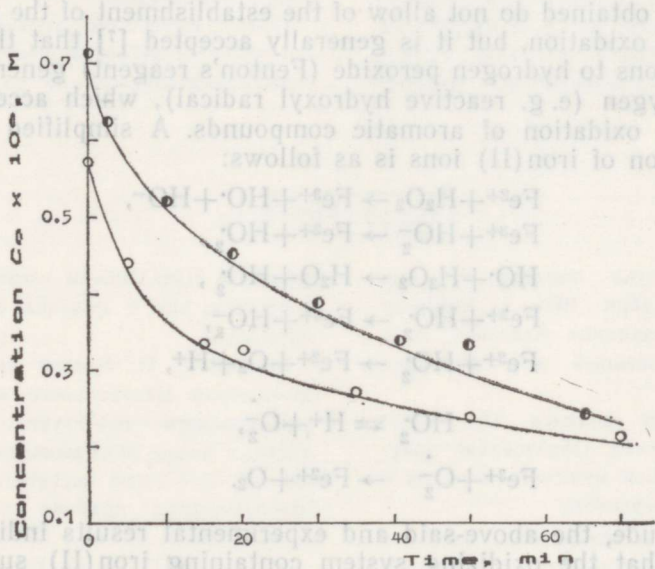


Fig. 2. Kinetics of carbazole oxidation by hydrogen peroxide in the presence of manganese(II) chloride at $25\pm 1^\circ\text{C}$.

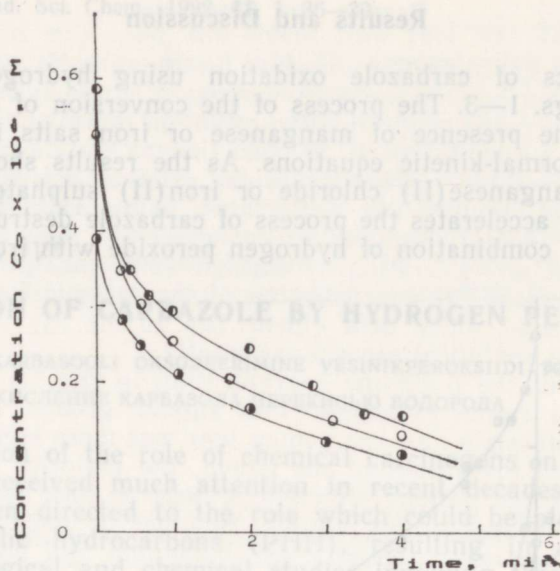
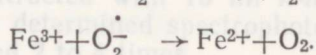
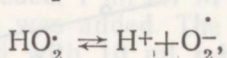
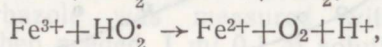
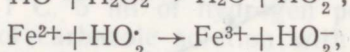
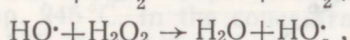
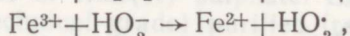
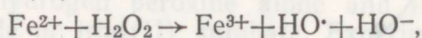


Fig. 3. Kinetics of carbazole oxidation by hydrogen peroxide in the presence of iron(II) sulphate at $25 \pm 1^\circ \text{C}$.

Initial concentration (C_0), molar ratio, and half-life ($\tau_{1/2}$) of carbazole degradation by different oxidizing systems at $25 \pm 1^\circ \text{C}$

Oxidizing system	$C_0 \times 10^7, \text{M}$	Molar ratio carb./salt/ H_2O_2	$\tau_{1/2}, \text{min}$
H_2O_2	5.76	1/ — / 10^3	1020
$\text{MnCl}_2 + \text{H}_2\text{O}_2$	5.72	$1/5 \times 10^2 / 10^3$	48
$\text{FeSO}_4 + \text{H}_2\text{O}_2$	5.87	$1/5 \times 10^2 / 10^3$	0.8

The data obtained do not allow of the establishment of the mechanism of carbazole oxidation, but it is generally accepted [7] that the addition of iron(II) ions to hydrogen peroxide (Fenton's reagent) generates active forms of oxygen (e.g. reactive hydroxyl radical), which accelerates for example the oxidation of aromatic compounds. A simplified scheme of the conversion of iron(II) ions is as follows:



To conclude, the above-said and experimental results indicate to the possibility that the oxidizing system containing iron(II) sulphate and hydrogen peroxide could be used in the process of the destruction of carcinogenic dibenzocarbazoles.

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Знания в Дрезденском техническом университете, где и получил степень доктора наук.
В 1944 г. О. Киррет был назначен директором Центрального научно-исследовательского института промышленности, нося в то время след. название: Институт промышленности, а в 1958 г. — Институт промышленности, а в 1960—1978 гг. О. Киррет был директором Института знаний и промышленности.

Эстонская наука получила известность 18 декабря 1981 г. восточный университет Академии наук Эстонии заслуженный деятель науки Оскар Киррет.
Оскар Киррет родился 27 ноября 1909 г. в Вильянди. Образование получил в Рижской мужской гимназии и Тартуском университете.
Свое трудовое деятельность он начал в 1938 г. в то время что открылся в Таллинском техническом институте. В 1938—1940 гг. совершенствовал свои