

**Zusammenfassung.** Der Erythrozyt hat zwei Hauptwege für den Glukoseabbau. Der Emden-Meyerhoff-Weg resultiert in der Phosphorylierung von ADP zu ATP und der Reduktion von  $\text{NAD}^+$  zu NADH. Der Hexose-Monophosphat-Weg ermöglicht andererseits die Reduktion von  $\text{NADP}^+$  zu NADPH. Es besteht

eine beachtliche Beweglichkeit in der Kontrolle dieser Bahnen, die es dem Erythrozyten ermöglichen, seine Enzyme und sein Hämoglobin in aktiver Form und das Konzentrationsgefälle von Natrium und Kalium zwischen roten Blutkörperchen und Plasma zu erhalten.

## SPECIALIA

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### Peroxides of Diisopropylether

Investigating the ozonisation of tetramethylethylene<sup>1</sup>, it was found desirable to have for comparison IR-spectra and Rf values of some suitable simple peroxide containing, besides the hydroperoxy, also an ether group. Such a compound, 2,2'-dihydroperoxy-2,2'-diisopropyl ether (I), was originally prepared by IVANOV, SAVINOVA and MICHAILOVA<sup>2</sup>. When peroxide I, prepared according to IVANOV et al., was analysed by the paper chromatographic method of MILAS and BELIČ<sup>3</sup>, 2 peroxydic spots in addition to  $\text{H}_2\text{O}_2$  were detected. Further confirmation of the presence of 2 peroxides was obtained by thin layer chromatography which was successfully used for the separation of peroxides by several authors<sup>4</sup>. Best separation was obtained with silikagel G and a mixture of toluene and methanol as used by BUZLANOVA et al.<sup>5</sup>. With this method also, 2 peroxides could be detected. The Table gives the Rf values obtained by the above chromatographic methods.

With the aid of preparative thin layer chromatography, both peroxides have been isolated in pure state and the purity of both was checked by tlc. The peroxide with the higher Rf value, suspected on the basis of its molecular weight and active oxygen content to be 2,2'-dihydroperoxy-2,2'-diisopropyl peroxide (II), was found to have an IR-spectrum and Rf values which were identical with

those of II prepared according to MILAS and GOLUBOVIĆ from acetone<sup>6</sup>. Therefore, the peroxide with the lower Rf was held to be I. It had the expected molecular weight and active oxygen content and solidified when kept for a few days at room temperature. After crystallizing from pentane, this solid peroxide was identified as 1,1,4,4,7,7-hexamethyl-1,4,7-cyclononatriperoxane by its melting point, Rf value and IR-spectrum. Peroxide II remained unchanged under the same conditions. It is known that only peroxides containing an ether group rearrange spontaneously, whereas peroxides containing peroxy groups do so only in the presence of strong acids<sup>1</sup>. The IR-spectra of the separated peroxides I and II also support the above conclusion, peroxide I showing strong bands at 1.042 and 988  $\text{cm}^{-1}$  which are absent in the IR-spectrum of II. Therefore, when a synthesis of peroxide I is attempted according to IVANOV et al. a mixture of I and II is obtained, as a consequence of which a chromatographic separation of pure I is necessary<sup>7</sup>.

**Zusammenfassung.** Stellt man 2,2'-Dihydroperoxy-2,2'-Diisopropyläther nach IVANOV et al. aus Isopropyläther her, so entsteht nebenbei auch noch 2,2'-Dihydroperoxy-2,2'-Diisopropyl-Peroxid. Beide Peroxide kann man papier- und dünnschichtchromatographisch nachweisen und mit präparativer Dünnschichtchromatographie rein isolieren.

I. BELIČ and T. SUHADOLC

Chemical Institute Boris Kidrič,  
Ljubljana (Yugoslavia), 2 January 1969.

Rf values of the peroxides of diisopropyl ether

|                                                                                                                                                                                                   | Dimethyl-<br>formamide-<br>decalin<br>(pc) | Butanol-<br>ethanol- $\text{H}_2\text{O}$<br>(pc) | Toluene-<br>methanol<br>(thin layer<br>chromat.) |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------|---------------------------------------------------|--------------------------------------------------|
| $\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\   \quad   \\ \text{HOO}-\text{C}-\text{O}-\text{C}-\text{OOH} \\   \quad   \\ \text{CH}_3 \quad \text{CH}_3 \\ \text{I} \end{array}$           | 0.01                                       | 0.75                                              | 0.24                                             |
| $\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\   \quad   \\ \text{HOO}-\text{C}-\text{O}-\text{O}-\text{C}-\text{OOH} \\   \quad   \\ \text{CH}_3 \quad \text{CH}_3 \\ \text{II} \end{array}$ | 0.13                                       | 0.84                                              | 0.64                                             |

<sup>1</sup> N. A. MILAS and I. BELIČ, Vest. Slov. kem. Društ. 10, 37 (1963).

<sup>2</sup> K. I. IVANOV, B. K. SAVINOVA, E. G. MIHAJLOVA, Zh. Obshch. Khim. 16, 16 (1946).

<sup>3</sup> N. A. MILAS and I. BELIČ, J. Am. chem. Soc. 81, 3358 (1959).

<sup>4</sup> E. STAHL, Dünnschicht-Chromatographie (Springer, Berlin 1967), p. 209, 633, 647.

<sup>5</sup> M. M. BUZLANOVA, V. F. STEPANOVSKAJA, V. L. ANTONOVSKY, Zh. analit. Khim. 21, 1492 (1966).

<sup>6</sup> N. A. MILAS and A. GOLUBOVIĆ, J. Am. chem. Soc. 81, 6461 (1959).

<sup>7</sup> The authors wish to thank Professor N. A. MILAS for his interest in this work. The financial support of the 'Boris Kidrič Fund' is gratefully acknowledged.