IMPROVED PROCEDURE FOR THE PREPARATION OF DIETHYL KETONE TRIPEROXIDE AND KINETICS OF ITS THERMAL DECOMPOSITION REACTION IN SOLUTION

G. N. Eyler, A. I. Cañizo, E. E. Alvarez, and L. F. R. Cafferata^{*}

Facultad de Ingeniería, Universidad Nacional del Centro de la Provincia de Buenos Aires, Olavarría, and Laboratorio de Compuestos Orgánicos (LADECOR), Universidad Nacional de La Plata, Calle 47 esq. 115, (1900) La Plata, República Argentina.

Abstract: Diethyl ketone triperoxide is obtained in a simple and efficient one-step procedure using the acid-catalysed oxidation reaction of diethyl ketone by hydrogen peroxide. Its thermolysis in toluene solution is initiated by a rate determining peroxidic bond rupture of that substituted triperoxane molecule.

When diethyl ketone reacts with hydrogen peroxide (*ca* 50 % concentration) in acetonitrile-sulphuric acid media at 0° C, a complex mixture of peroxidic compounds is obtained. In this case diethyl ketone bis (hydroperoxy) peroxide (I) is the most abundant species (85% yield) and 1,1,4,4,7,7-hexaethyl-1,4,7--cyclononatriperoxane (II) the secondary reaction product (12 % yield). However, the isolated peroxide (I) in the presence of diethyl ketone and concentrated sulphuric acid leads to the substituted hexoxonane (II) in quantitative yields.¹ Brune *et al.* employed the same reaction, but with a slightly different procedure at the above temperature they obtained 3,3,6,6-tetraethyl-1,2,4,5-tetroxane (III) (31 % yield).²



CID

1746

We now report an improved procedure for the preparation of (II) including kinetic data for its thermolysis in solution. In this work diethyl ketone (50 mmole) was added dropwise with stirring to a mixture of hydrogen peroxide (30 % concentration, 56 mmole) and sulphuric acid (70 % v/v concentration, 14 α) at -10⁰ C. After 3 h of reaction, the mixture was extracted twice with purified light petroleum ether and the organic laver freed of excess hydrogen peroxide with aqueous ammonium sulfate and water washings, and then dried over anhydrous sodium sulfate. The solution was evaporated at low pressure and room temperature and the residue left overnight in a desiccator. The translucid solid obtained was twice recrystallized from boiling methyl alcohol. The colorless crystals (m p $59-60^{\circ}$ C: lit¹ $58-59^{\circ}$ C for (II). 80 % yield), actually corresponded to 1.1.4.4.7.7 - hexaethyl - 1.4.7 cyclononatriperoxane, according to its IR spectrum.¹ The TLC of this compound on silica gel and alumina "Merck" F₂₅₄-aluminium sheets showed singlet spots in both adsorbents with R, of 0.6 and 0.8, respectively, using benzene as eluting solvent. Kinetic experiments on the thermal decomposition reaction of (II) in tolugne solution (ca 0.02 M) in the 130° to 160° C temperature range were carried out using the ampoules technique. ³ Bibenzyl (this compound originated from the reaction solvent) and diethyl ketone, in this order of vields, were the most important products of the thermolysis. No induced decomposition reaction of (II) in the above experimental conditions was detected and first order rate constant values were obtained to at least 40 % triperoxide conversion. At 145° C, the k value was 6.6 \times 10⁻⁵ s⁻¹ and the activation parameters of the initial unimolecular reaction ($\Delta H^{\ddagger} = 37.0 \pm 1.7$ kcal sole⁻¹: $\Delta S^{\ddagger} = 12.2 \pm 4.2$ cal sole⁻¹ K⁻¹) are reasonable values for a peroxidic bond rupture in that type of molecule. Similar but less extensive kinetic studies on the thermolysis of (II) were done in benzene, and the rate constant value at 120⁰C is similar to that extrapolated in toluene solution. Capillary GC (with FID detection) employing a 30 m methyl silicone fused silica column (at 150⁰C) was used for monitoring (II) and the above products after selected times of reaction.

Acknowledgment. This work was financially supported by the Universidad Nacional del Centro de la Provincia de Buenos Aires and, in part, by INIFTA. References

1. Milas, N.A.; Golubovic, A. J. Am. Chem. Soc., 1959, 81, 3361.

2. Brune, H.A.; Wulz, K.; Hetz, W. Tetrahedron, 1971, 27, 3629.

3. Cafferata, L.F.R.; Mirífico, M.V.; Eyler, B.N. J. Org. Chem., 1984, 49, 2107.

(Received in USA 21 January 1992; accepted 4 January 1993)