Tetrahedron. Vol. 34, pp. 1231 to 1233. Pergamon Press 1978. Printed in Great Britain

ORGANIC PEROXIDES—XIX[1]

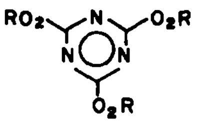
DECOMPOSITION OF TRIALKYLPEROXY TRIAZINES

H. Kropf* and H. Mirzai Amirabadi
Institute of Organic Chemistry and Biochemistry, University Hamburg, D 2000 Hamburg,
Martin-Luther-King Platz 6, Deutschland

(*Received in the UK* 19 *September* 1977; *Accepted for publication* 6 *October* 1977)

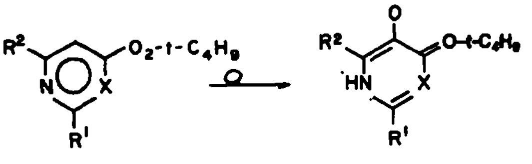
Abstract—The kinetics of the decomposition of tri-t-butylperoxy-1,3,5-triazine (from trichloro-1,3,5-triazine and barium t-butyl peroxide *in situ*) follows the 1-order with an activation energy of 24.6 kcal/mole. Isolated products are cyanuric acid and acetone. The reaction of trichloro-triazine with potassium cumyl peroxide yields cyanuric acid, isopropenyl phenyl ether, dicumyl peroxide, acetone and phenol, with barium 2-benzyl-2-propyl peroxide cyanuric acid, benzaldehyde and 2-benzyloxy-2-[2-benzyl-2-propylperoxy]-propane. The mechanism of the decomposition is discussed.

In 1972 Sokolov *et al.*[2] reported the synthesis of the surprisingly stable tri-t-butylperoxy-1,3,5-triazine (**1a**) (90% decomposition after 2 hr in nonane at 140°). Tricumylperoxy-1,3,5-triazine (**1b**) was not isolable. It was completely destroyed after 12 hr at 20°. Reaction products (after acidification) were acetone (75%) and phenol (82%). A mechanism analogous to the Criegee rearrangement was proposed for the decomposition of **1b**.



Ia $R = t\text{-}C_4H_9$—
Ib $R = C_6H_5\text{-}C(CH_3)_2$—

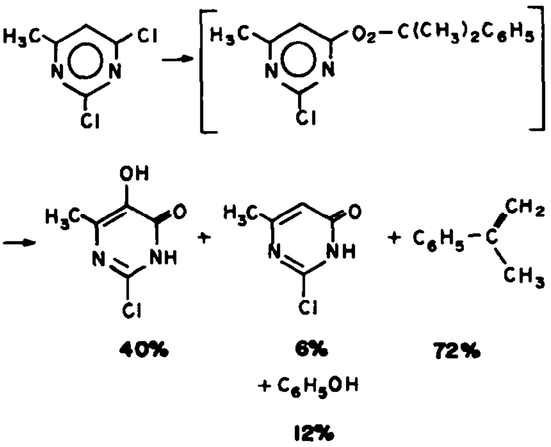
Contrarily we have proved a radical cage reaction for the rearrangements of 4-t-butylperoxy-6-methyl-pyrimidine (**2a**), 4-t-butylperoxy-2-chloro-6-methylpyrimidine (**2b**) and ethyl 4-t-butylperoxy-2-chloro nicotinate (**2c**) (from barium t-butyl peroxide and the corresponding 4-chloro heterocycles) to the pyrimidones **3a** and **3b** and to the pyridone **3c** (3 weeks at 20°; yield 55–85%)[3] respectively.



2 **3**

(a) X = >N R^1 = H, R^2 = CH_3
(b) X = >N R^1 = Cl, R^2 = CH_3
(c) X = >C–$CO_2C_2H_5$ R^1 = Cl, R^2 = H

In the reaction of the 4-chloro heterocycles with sodium cumyl peroxide we obtained only the scission products of the intermediary peroxides, showing a mainly radical rearrangement besides a minor ionic reaction (~6–7:1), for instance:



Because of the different results relative to the stability of the peroxides (with the same alkyl group) and to the mechanism of the rearrangement we have reexamined the work of Sokolov *et al.*,[2] and we also tested the reaction of trichloro-1,3,5-triazine with barium 2-benzyl-2-propyl peroxide.

Compound **1a** was obtained by the method described[3] in 80.5% yield from trichloro-1,3,5-triazine and barium t-butyl peroxide *in situ* (m.p. 57–58° lit.[2] 48–50°; in the IR spectrum we observed considerable shifts of the peaks relative to the reports of Sokolov *et al.*[2]). The kinetics of the decomposition of **1a** ($c_0 = 1$ mmole/l in *o*-dichlorobenzene; followed by the disappearence of the ^1H NMR signal of the methyl protons at $\tau = 8.72$ ppm, simultaneously a new signal appearing at $\tau = 8.09$ ppm originating from acetone as decomposition product) could be ascertained only above 100°. The reaction followed the 1-order with the rate constants

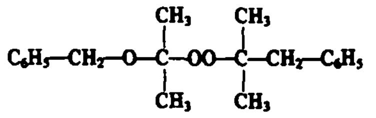
$$k_{110} = 2.53 \times 10^{-5}\ [\mathrm{sec}^{-1}]$$
$$k_{125} = 9.94 \times 10^{-5}\ [\mathrm{sec}^{-1}]$$
$$k_{135} = 23.18 \times 10^{-5}\ [\mathrm{sec}^{-1}]$$
$$k_{140} = 45.29 \times 10^{-5}\ [\mathrm{sec}^{-1}]$$
$$k_{154} = 58.65 \times 10^{-5}\ [\mathrm{sec}^{-1}].$$

The activation energy was calculated as

24.6 kcal/mole. A decomposition to radicals was not demonstrable by ESR spectroscopy. Isolated decomposition products were cyanuric acid (60.8%) and acetone (37.2% as 2,4-dinitrophenylhydrazone).

In the reaction of trichloro-1,3,5-triazine with potassium cumyl peroxide (0° in petrol ether) a peroxide could not be isolated but shown as intermediate by TLC analysis (DC-alufolie, Kieselgel 60 F 254, with spray reagent for peroxides[4]—violet colour after a few minutes). Isolated products were cyanuric acid (88%), isopropenyl phenyl ether (47.5%), dicumyl peroxide (8.9%), acetone (38.6% as 2,4-dinitro phenyl hydrazone) and phenol (6.8%, bromometric determined).

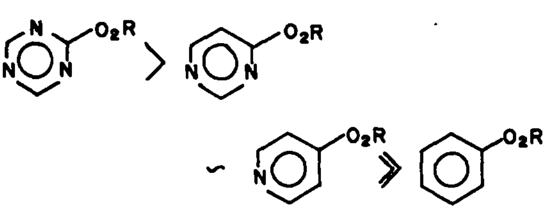
Also in the reaction of trichloro-1,3,5-triazine with barium 2-benzyl-2-propyl peroxide *in situ* we observed a peroxidic product by TLC analysis, which decomposed in the course of the reaction giving another peroxide identified as 2-benzyloxy-2-[2-benzyl-2-propylperoxy]-propane 4[5] (33.1%). In addition, we isolated cyanuric acid (63.4%) and benzaldehyde (65.5%).



$C_6H_5{-}CH_2{-}O{-}C(CH_3)_2{-}OO{-}C(CH_3)_2{-}CH_2{-}C_6H_5$ 4

DISCUSSION

In confirmation of the results of Sokolov *et al.*[2] alkylperoxy triazines proved to be more stable than peroxides derived from pyrimidine, pyridine[3] and benzene:[6]



Likewise the relation of ionic to radical rearrangement respectively decomposition shifts. From alkylperoxy triazines products of an ionic decomposition were obtained as main products. With alkylperoxypyrimidines and pyridines the radical cage rearrangement preponderated;[3] alkylperoxy benzenes decomposed exclusively in a radical manner.[6]

Indeed radicals were not detected in the decomposition of 1a by ESR spectroscopy, however a partly radical reaction is not to be excluded since 1b reacts 10% in this manner. But 1b should tend more to the Criegee rearrangement than 1a. The partly radical decomposition of 1b was demonstrated by the formation of dicumyl peroxide.[7]

The formation of 4 in the reaction of trichlorotriazine with barium 2-benzyl-2-propyl peroxide follows an ionic mechanism analogously to the reaction of the peroxide with benzenesulfonyl chloride.[5] The mechanism of the formation of benzaldehyde is not yet clarified. Indeed benzaldehyde is a product of the thermal decomposition of 2-benzyl-2-propyl hydroperoxide, but we did not find dibenzyl in this case as expected.[5]

It is to be remarked, that the relative stability of the trialkylperoxy triazines and their tendency to an ionic decomposition is not related to the pK-values of the corresponding phenols or a blocking effect of the *o*-, *o'*-positions.[7]

EXPERIMENTAL

The ^1H NMR spectra were recorded with the Varian T 60 and NV 40 with TMS as internal standard. The IR spectra were taken with a Perkin–Elmer 257.

Tri-t-butylperoxy-1,3,5-*triazine* (1a). To a stirred suspension of barium oxide (9.7 g) in 50 ml petrol ether (30–50°) was dropped under ice cooling a soln of t-butyl hydroperoxide (1.5 g; 16.6 mmoles) in 20 ml petrol ether and then at room temp. a stirred mixture of t-butyl hydroperoxide (5.25 g; 58.3 mmoles) and trichlorotriazine (4.6 g; 25 mmoles) in 60 ml petrol ether. After 3 hr no trichlorotriazine was detected by TLC. The mixture was filtered, the solvent removed and the residue dissolved in dichloromethane. Dilution with petrol ether and standing in a refrigerator gave 2.72 g tri-t-butylperoxy-1,3,5-triazine (80.5%) m.p. 57–58°; IR spectrum see Fig. 1. (Found: C, 52.16; H, 7.80; N, 12.24. Calc. for $C_{12}H_{27}O_6N_3$: C, 52.17; H, 7.82; N, 12.17%).

Decomposition of 1a. A soln of 1a (1 g; 2.9 mmoles) in 30 ml *o*-dichlorobenzene was heated in a slow N_2 stream for 4 hr at 140°. After a short time the mixture turned light yellow, then light brown, while a ppt deposited. After cooling to room temp. one half of the mixture was extracted 4x with 10 ml water and in the collected water phases acetone was determined as 2,4-dinitrophenylhydrazone: 194 mg (total 37.4%) m.p. 125–6°. The second half of the mixture was filtered and the residue recrystallized from EtOH: 228 mg cyanuric acid (total 60.8%) m.p. 350° (d).

Reaction of trichloro-1,3,5-*triazine with potassium cumyl peroxide.* To a stirred and ice cooled suspension of potassium cumyl peroxide[8] (10.2 g; 60 mmoles) in 50 ml petrol ether a stirred suspension of trichlorotriazine (3.6 g; 20 mmoles) was added during 1 hr. TLC analysis showed a peroxidic product as intermediate. After 3 hr the trichlorotriazine had reacted completely. The mixture was filtered. Recrystallisation of the residue from EtOH yielded 1.3 g cyanuric acid (88%), m.p. 350° (d). The filtrate was diluted in a volumetric flask with petrol ether. Acetone was determined in an aliquot part as 2,4-dinitrophenyl hydrazone:

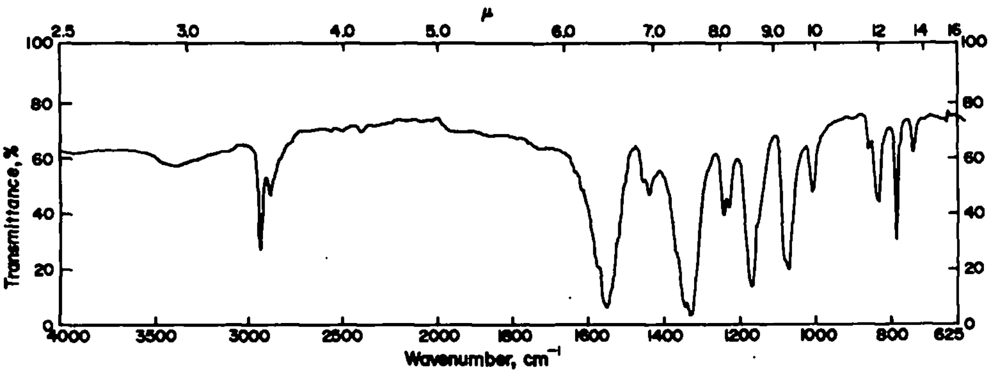


Fig. 1. IR spectrum of tri-t-butylperoxy-1,3,5-triazine (KBr).

38.6% m.p. 125°, phenol bromometric: 6.8%. The remaining soln was extracted repeatedly with 20% NaOHaq, the water phases acidified and extracted with ether. After drying and removing the ether phenol was obtained, m.p. 39°. The petrol ether phase was dried and the petrol ether removed. Distillation of the residue yielded 1.9 g isopropenyl phenyl ether (total 47.5%) b.p. 18°/0.05 Torr, identified by IR and NMR spectra). Chromatography of the residue on silica yielded 460 mg dicumyl peroxide (total 8.9%) m.p. 34.5°.

Reaction of trichloro-1,3,5-*triazine with barium* 2-*benzyl*-2-*propyl peroxide.* To a stirred suspension of barium oxide (6.0 g; 40 mmoles) in 50 ml petrol ether (30–50°) a soln of 2-benzyl-2-propyl hydroperoxide (0.3 g; 2.3 mmoles) in 30 ml petrol ether was added under ice cooling, then simultaneously at room temp. a soln of hydroperoxide (2.1 g; 12.6 mmoles) in 50 ml petrol ether and a stirred suspension of trichlorotriazine (0.92 g; 5 mmoles) in 80 ml petrol ether. TLC showed a peroxide, which disappeared as the reaction proceeded and, another peroxide was observed. After 10 hr the reaction was filtered. Extraction of the residue with EtOH yielded 408 mg cyanuric acid (63.4%) m.p. 350° (d). From the filtrate the solvent was removed. Distillation of the residue yielded benzaldehyde (2.1 g; 65.6%) b.p. 176–178°, m.p. of the 2,4-dinitrophenyl hydrazone 230–233°. The residue was cleaned by LC yielding 520 mg 2-benzyloxy-2-[2-benzyl-2-propylperoxy]-propane (33.1%), identified by IR and NMR spectra.

Acknowledgements—We thank the Verband der Chemischen Industrie Fond der Chemischen Industrie for a support, H. M. A. thanks the Konrad–Adenauer–Stiftung for a scholarship.

REFERENCES

[1] Part XVIII: H. Kropf, R. Schröeder and R. Fölsing, *Synth.* 894 (1977).
[2] N. A. Sokolov, L. G. Usova, N. N. Vyshinsky and O. S. Morozvo, *Zh. Obshch. Kim.* 42, 2074 (1972), *Chem. Abstr.* 78, 29728 (1973).
[3] H. Kropf and M. Ball, *Liebigs Ann.* 2331 (1976).
[4] W. Huber and E. Fröhlke, *Chromatographie* 5, 256 (1972).
[5] H. Kropf and C.-R. Bernert, *Liebigs Ann.* 751, 109 (1971).
[6] t-Butyl peroxy benzene from the reaction of diphenyl bromonium tetrafluoroborate with sodium t-butyl peroxide is not traceable, it rearranges directly to *o*- and *p*-t-butoxyphenol (H. Kropf, M. Ball and R. Sievers, unpublished).
[7] H. Kropf, M. Ball, H. Siegfriedt and S. Wagner, in preparation.
[8] N. A. Sokolov, L. G. Usova and V. A. Shushumov, *J. Gen. Chem. USSR* 40, 190 (1970).