J. inorg. nucl. Chem., 1975, Vol. 37, pp. 2507–2508. Pergamon Press. Printed in Great Britain

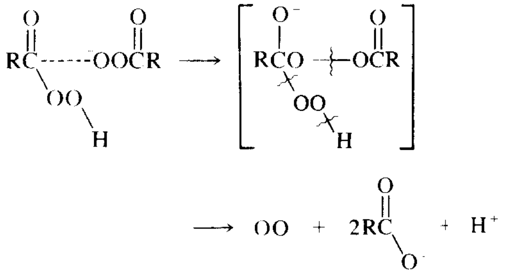
BASE-CATALYZED DECOMPOSITION OF *p*-NITROPEROXOBENZOIC ACID

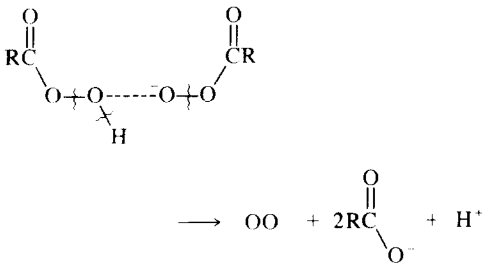
K. G. SAUNDERS[1a], R. T. STADNICKI[1b] and J. E. McISAAC, Jr.
Western New England College, 1215 Wilbraham Road, Springfield, MA 01119, U.S.A.

(*Received* 2 *December* 1974)

Abstract—The base-catalyzed decomposition of *p*-nitroperoxobenzoic acid has been studied using a double isotope labeling technique. The decomposition of a sample of the peroxo acid in which 2·3% of the peroxidic oxygen was doubly labeled as $-^{18}O-^{18}O-$ led to complete retention of the double label in the product oxygen, $^{36}O_2$. This result is consistent with a decomposition mechanism involving nucleophilic attack of the conjugate base of *p*-nitroperoxobenzoic acid upon the carbonyl carbon of the undissociated acid.

THE base-catalyzed decomposition of peroxocarboxylic acids to parent acids and oxygen has been studied by several groups of researchers[2–6]. Tracer experiments[3–6] using double ^{18}O labeling of the peroxidic oxygens are consistent with the postulate that these acids may decompose simultaneously *via* two distinctly different paths: (1) involving nucleophilic attack by the peroxo acid anion upon the carbonyl carbon of the peroxo acid, and (2) involving nucleophilic attack of the anion upon the outer oxygen of the peroxo acid. Path (1) leads to complete retention of the double label (no scrambling) whereas path (2) leads statistically to complete loss of the double label (scrambling). For example, peroxoacetic acid decomposes 83% by path (1) and 17% by path (2)[4]. When the carbonyl site is sterically hindered, as in the case of peroxopivalic acid[6], the results are reversed (Table 1).


(1)


(2)

The data of Table 1 indicate that, in the absence of steric hindrance, carbonyl carbon is the preferred, but not exclusive, site of attack. We chose to study the decomposition of *p*-nitroperoxobenzoic acid. This acid was selected because of the ability of the *p*-nitro group to facilitate nucleophilic attack at benzo carbon[7].

The synthesis of doubly labeled monoperoxophthalic acid from the parent acid anhydride has been reported[5]. However, due to the aqueous insolubility of *p*-nitrobenzoic anhydride, this method is not suitable for the preparation of doubly labeled *p*-nitroperoxobenzoic acid. A satisfactory modification of this synthesis was developed using a mixed solvent of tetrahydrofuran-water. Repeated syntheses yielded mixtures of the peroxo acid and parent acid of 45% and 55% respectively. Analysis of the product by both base and iodometric titration[8] confirmed that it contained only peroxo acid and parent acid. Figure 1 is a typical titration curve of a sample of *p*-nitroperoxobenzoic acid. The data give pK_a *p*-nitroperoxobenzoic acid = 7·1, and pK_a *p*-nitrobenzoic acid = 3·4, which agree well with published values of 7·1[9] and 3·3[10] respectively.

The base catalyzed decomposition of a sample of *p*-nitroperoxobenzoic acid in which 2·3% of the peroxidic oxygen was doubly labeled as $-^{18}O-^{18}O-$ was carried out at room temperature in a phosphate buffer at pH = 7·1. The results are given in Table 2. The oxygen gas evolved

Table 1. Results of double labeling tracer experiments

Acid	Attack on O, %	Attack on C, %
Peroxoacetic	17	83
Monoperoxophthalic	74	26
Peroxopivalic	76	24

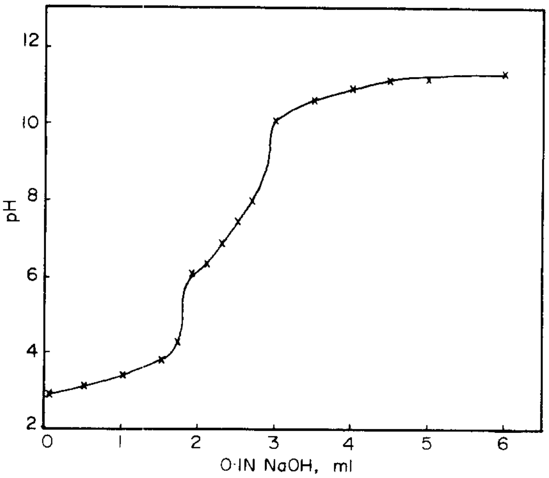


Fig. 1. Titration curve for *p*-nitroperoxobenzoic acid.

Table 2. Mass spectral analysis of oxygen gas

	Peak Heights		
	$^{32}O_2$	$^{34}O_2$-	$^{36}O_2$
I. H_2O_2[a]			
Oxygen	2,551	15.5	59.6
Oxygen %	97.1	0.59	2.27
II. p-Nitroperoxobenzoic Acid[b]			
Oxygen	541	3.4	13.2
Oxygen %	97.0	0.61	2.37
% unscrambled = $\frac{2.37}{2.27}$ x 100 = 104			

(a) Oxygen liberated by ceric (IV) oxidation of H_2O_2 in 20% H_2SO_4 at room temperature [5].

(b) In the presence of 1 x 10^{-3}M EDTA to limit possible trace metal-catalized decomposition.

as $^{36}O_2$ is consistent with 104%[11] of the decomposition occurring by attack on carbonyl carbon, path (1).

We were thus able to promote exclusive attack at carbonyl carbon[12]. This result further confirms the existence of dual pathways for the decomposition of peroxocarboxylic acids. Indeed, the observation of complete retention of the double label indicates that there is no unseen mechanism leading to scrambling in these systems. This is substantial evidence supporting the results and conclusions for the peroxocarboxylic acids in which scrambling has been observed[13].

EXPERIMENTAL

Doubly labeled $H_2{}^{18,18}O_2$ was prepared by passing ^{18}O enriched H_2O (98 atom % ^{18}O, Miles-Yeda Ltd., Lot NO. 51–080A) through an electrical discharge tube[14]. The product $H_2{}^{18,18}O_2$ was rinsed from the cold traps with normal 90% H_2O_2 such that the resulting peroxide solution had an isotopic enrichment of 2·6 atom % ^{18}O.

p-Nitroperoxobenzoic acid was synthesized from the anhydride (prepared by dehydration of the acid with acetic anhydride and recrystallization from anhydrous ethyl acetate), m.p. 193–194° uncorrected. The anhydride was added to a solution of 0·5 g NaOH in 55 ml of tetrahydrofuran, freshly distilled from $KMnO_4$, and 15 ml of deionized water. The deionized water was obtained by passing distilled water through a Barnsted mixed-bed ion exchange column. The temperature was then lowered to − 20° in an acetone-dry ice bath. This was followed by the slow addition, with rapid stirring, of 1·1 ml of 90% H_2O_2. The reaction mixture was stirred at − 20° for 5 min and then quenched with the addition of 100 ml of cold 20% H_2SO_4. The products were extracted immediately with 100 ml of ether. The ether extract was evaporated under vacuum leaving a yellow slurry. The yellow residue was then dissolved in the smallest possible amount of ether. The ethereal solution was decanted from any insoluble matter, treated dropwise with cold pentane to the cloud point and crystallized at 0°. The resulting mixture of peroxo acid and parent acid was filtered and dried under vacuum.

Gas samples from the decompositions of both hydrogen peroxide and *p*-nitroperoxobenzoic acid were collected at approximately 100 torr at room temperature. Mass spectrometric analyses were performed on a Hitachi Perkin-Elmer RMU-6H instrument.

Acknowledgements—This work was supported by the Department of Chemistry, Western New England College. We wish to thank Peter Uden, University of Massachusetts, for the mass spectral analyses and J. O. Edwards, Brown University, for the use of the discharge tube.

REFERENCES

1a, 1b. Undergraduate research participants.

2. J. F. Goodman, P. Robson and E. R. Wilson, *Trans. Faraday Soc.*, **58**, 1846 (1962).
3. E. Koubek, G. Levy and J. O. Edwards, *Inorg. Chem.* **3**, 1331 (1964).
4. E. Koubek, M. L. Haggett, C. J. Battaglia, K. M. Ibne-Rasa, H. Y. Pyun and J. O. Edwards, *J. Am. Chem. Soc.* **85**, 226 (1963).
5. R. E. Ball, J. O. Edwards, M. L. Haggett and P. Jones, *Ibid.* **89**, 2331 (1967).
6. E. Koubek and J. E. Welsch, *J. Org. Chem.* **33**, 445 (1968).
7. J. Hine, *Physical Organic Chemistry*, p. 295. McGraw-Hill, New York (1962).
8. F. P. Greenspan and D. G. MacKeller, *Anal. Chem.* **20**, 1061 (1948).
9. J. E. McIsaac, Jr., L. R. Subbaraman, J. Subbaraman, H. A. Mulhausen and E. J. Behrman, *J. Org. Chem.* **37**, 1037 (1972).
10. A. Albert and E. P. Serjeant, *Ionization Constants of Acids and Bases*, p. 127. Wiley New York (1962).
11. This value is within the error limits of the technique. R. E. Ball, Ph. D. Thesis, p. 114. Brown University (1967).
12. It has been suggested[6] that, for peroxobenzoic acid, loss of conjugation following attack at carbonyl carbon should favor attack at oxygen to a greater extent than is found for peroxoacetic acid. In our case the powerful ability of the *p*-nitro group to stabilize a negatively charged transition state must be the dominant factor.
13. Also, the data further support the conclusions in related systems, J. E. McIsaac, Jr., R. E. Ball and E. J. Behrman, *J. Org. Chem.* **36**, 3048 (1971).
14. R. E. Ball, J. O. Edwards and P. Jones, *J. Inorg. Nucl. Chem.* **28**, 2458 (1966).