

$\text{PaX}_5 + n\text{H}_3\text{O}^+ + (n+1)\text{Cl}^- \rightarrow \text{H}_n\text{PaCl}^{-(n+1)}$
 where X represents a chloride, hydroxide or one-half oxide ion.

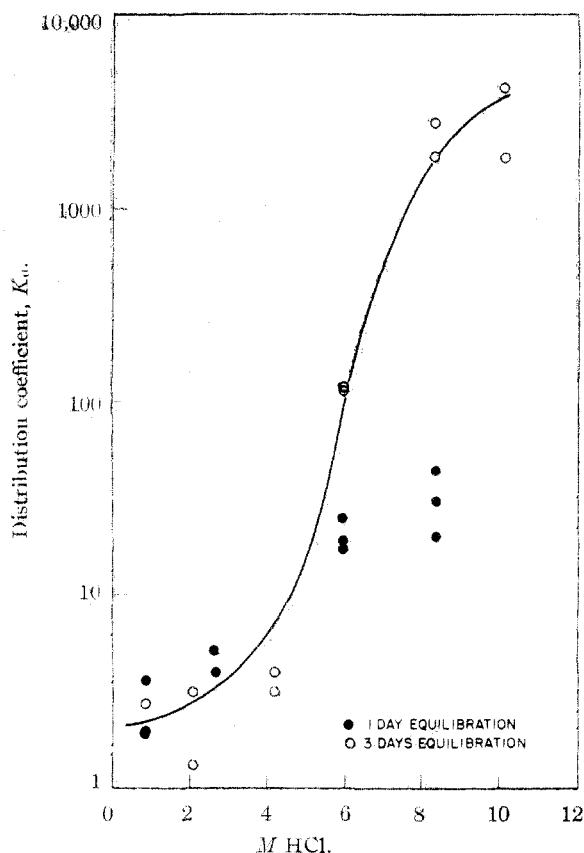


Fig. 1.—Adsorption of Pa(V) on Dowex-1 from chloride solutions.

Column Experiments.—The rapid change of K_d with hydrochloric acid concentration and the low values of K_d at low concentration make it very tempting to use anion exchangers for the purification of protactinium from metal ions particularly under conditions where they have different charges. The usefulness of such methods would depend on the reversibility of the adsorption and complexing processes during the elution time. To establish this reversibility a number of column experiments were carried out and it was found that protactinium at tracer concentrations can be quantitatively adsorbed from 8 M hydrochloric acid and washed with large numbers of column volumes of acid of this concentration without moving the band appreciably along the column and furthermore that the protactinium can be eluted with hydrochloric acid of lower concentration. The width of the elution band and the elution time were found to decrease with decreasing hydrochloric acid concentration of the eluent. Reasonably sharp elution bands were found for hydrochloric acid concentrations less than ca. 4M.

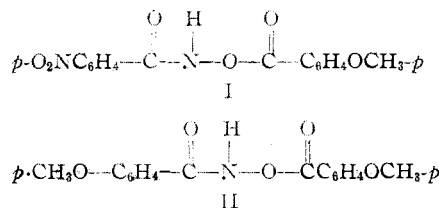
Acknowledgment.—The helpful advice and interest of Dr. George E. Boyd in this work is gratefully acknowledged.

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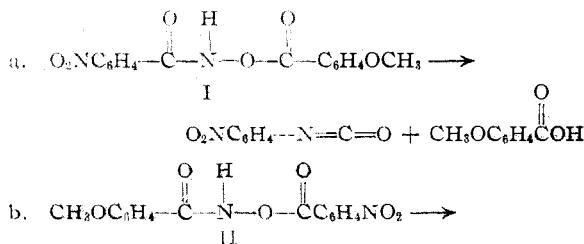
The Decomposition of Diacylhydroxylamines

BY JOHN E. LEFFLER

It has been shown recently that *p*-methoxy-*p'*-nitrobenzoyl peroxide decomposes, under favorable conditions, by a polar mechanism involving rearrangement of an assumed oxygen cation intermediate.¹ The favorable conditions required are a medium of high dielectric constant or an acid catalyst. Since the diacyl peroxide rearrangement superficially resembles the Lossen rearrangement, it was of interest to examine the two diacylhydroxylamines (I and II) derived from the peroxide by replacing one oxygen atom by an imino group.

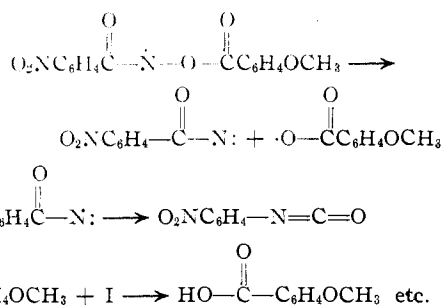
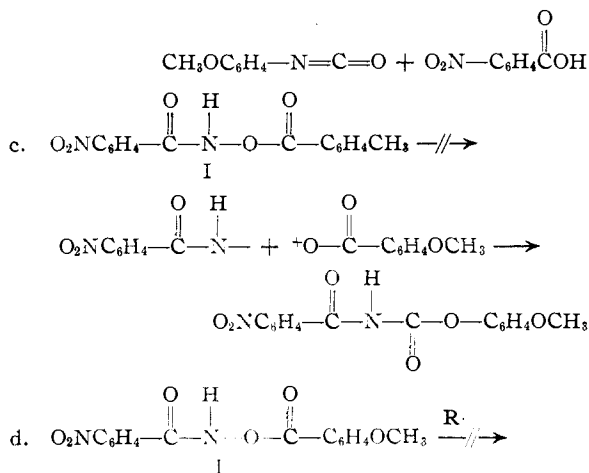


Both of the nitrogen analogs are considerably more stable than the peroxide; they can be recrystallized from hot polar solvents. Heating in nitrobenzene at 150–170° decomposes them but the reaction follows the path of the Lossen rearrangement (reactions a and b) in both cases. There is no tendency for I to give anisoyloxy cations (reaction c). When I is refluxed with dioxane and concentrated hydrochloric acid, it is merely hydrolyzed to anisic and *p*-nitrobenzoic acids. Nor is I sensitive to the action of free radicals from anisoyl peroxide; thus a radical chain decomposition (reaction d) starting with the removal of an atom of hydrogen from the imino group may be ruled out. Such a reaction would be analogous to the observed base-catalyzed Lossen rearrangement in which a proton is removed from the imino group.²



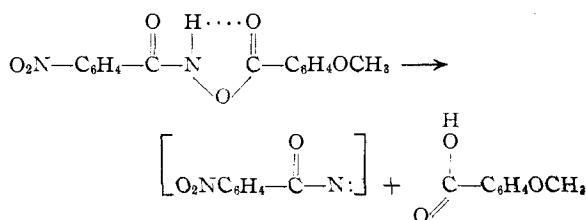
(1) Leffler, *THIS JOURNAL*, **72**, 67 (1950).

(2) Renfrow and Hauser, *ibid.*, **59**, 2309 (1937).



The infrared absorption spectrum of II (Fig. 1) has a weak band at 3280 wave numbers, probably due to an N-H vibration.^{3a} Since the alternative assignment, an OH vibration, is ruled out by the absence of a band in the C=N region (1700 to 1670 wave numbers) and since the band at 1645

wave numbers is typical of the group -N(H)-C(=O)- , the hydrogen is located on the nitrogen rather than on the carbonyl oxygen.^{3b} But the possibility of hydrogen bonding to a carbonyl is not ruled out and this suggests an explanation for the stability of these diacylhydroxylamines and a mechanism for their decomposition in neutral media



Experimental

N-Anisoyl-O-(p-nitrobenzoyl)-hydroxylamine.—To a suspension of 13 g. of the barium salt of anisidroxamic acid in 70 cc. dioxane (made by the general method of Renfrow and Hauser³) is added 10.3 g. of p-nitrobenzoyl

(3a) Using a Nujol (mineral oil) paste.

(3b) Randall, Fowler, Fuson and Daugl, "Infrared Determination of Organic Structures," D. Van Nostrand Co., New York, N. Y., 1949.

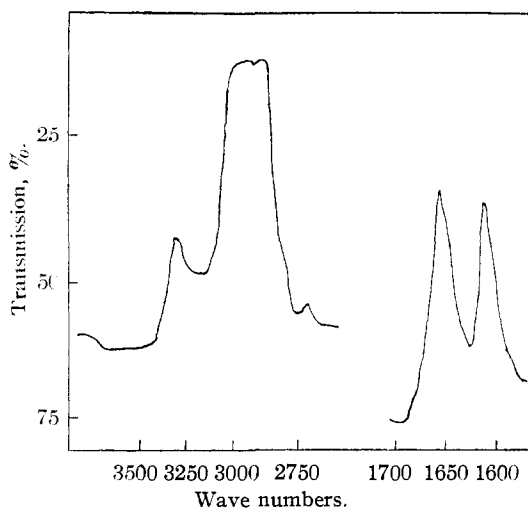


Fig. 1.

chloride. The mixture is boiled for five minutes, cooled to room temperature and poured into 900 cc. of water. The resulting precipitate, crystallized from dilute ethanol, gives 7.1 g., m. p. 140–145° d. Recrystallization several times from acetone-pet. ether raised the melting point to 164–165° (decomposes and resolidifies). *Anal.* Calcd. for $\text{C}_{15}\text{H}_{12}\text{O}_6\text{N}_2$: C, 56.9; H, 3.82; N, 8.85. Found⁴: C, 56.77, 56.56; H, 3.86, 3.79; N, 8.59, 8.54.

O-Anisoyl-N-(p-nitrobenzoyl)-hydroxylamine.—To a suspension of 20 g. of the barium salt of p-nitrobenzhydroxamic acid in 100 cc. dioxane is added 13.6 g. of anisoyl chloride. The mixture is boiled for five minutes, cooled, and poured into one liter of water, precipitating 23 g. of the crude product. Crystallization from acetone-pet. ether, from benzene, and from alcohol gave material melting at 187–188° (decomposes and resolidifies). *Anal.* Calcd. for $\text{C}_{15}\text{H}_{12}\text{O}_6\text{N}_2$: C, 56.9; H, 3.82; N, 8.85. Found⁴: C, 57.03, 57.33; H, 4.01, 3.81; N, 8.91, 8.99.

Decomposition of N-Anisoyl-O-(p-nitrobenzoyl)-hydroxylamine.—A solution of 0.44 g. of N-anisoyl-O-(p-nitrobenzoyl)-hydroxylamine in 10 cc. of nitrobenzene was heated for five minutes at 170° and then allowed to cool; a precipitate formed. The mixture was washed with 10% NaHCO_3 , dissolving the precipitate. Acidification of the NaHCO_3 extract gave 0.18 g. of p-nitrobenzoic acid, m. p. 236–239°, not depressed by an authentic sample. The nitrobenzene layer, refluxed for one hour with concentrated HCl, gave ca. 0.05 g. of p-anisidine, m. p. 55°, not depressed by an authentic sample.

Decomposition of O-Anisoyl-N-(p-nitrobenzoyl)-hydroxylamine.—A solution of 0.28 g. of O-anisoyl-N-(p-nitrobenzoyl)-hydroxylamine in 10 cc. of nitrobenzene, kept at 150–170° for fifteen minutes, gave 0.10 g. of anisic acid, m. p. 183–184.5°, not depressed by an authentic sample. A solution of 0.91 g. of O-anisoyl-N-(p-nitrobenzoyl)-hydroxylamine in 30 cc. of dioxane was refluxed two hours with 7 cc. of concd. HCl, evaporated to dryness and extracted with 10% NaHCO_3 giving 0.83 g. of acid, m. p. 215–224.5°, mixed with p-nitrobenzoic acid, ca. 230–235°. An equi-molar mixture of anisic and p-nitrobenzoic acids melts at 224.5° (end of melting). A mixture of 0.82 g. O-anisoyl-N-(p-nitrobenzoyl)-hydroxylamine and 0.03 g. anisoyl peroxide was refluxed under nitrogen for three hours in 60 cc. of benzene, then concentrated to 15 cc. and allowed to crystallize, giving 0.78 g. of unchanged O-anisoyl-N-(p-nitrobenzoyl)-hydroxylamine, m. p. 184–185° d. (resolidifies).

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RECEIVED APRIL 10, 1950

(4) Analyses by Clark Microanalytical Laboratory.